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CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS

ERNEST MERRITT, and FREDERICK BEDELL

CLXX

JUNE, 1910

Studies in Thermo-Luminescence. III. The Distribution of Energy in the Luminescence Spectrum of Sidot Blende. C. A. PIERCE 663

On the Extra Transmission of Electric Waves. F. C. BLAKE 674

Magnetostriction in Iron-Carbon Alloys. HERBERT G. DORSEY 698

The Point Discharge in Air for Pressures Greater than Atmospheric. O. AMSDEN GAGE 720

The Physical Properties of Binary Liquid Mixtures. J. C. HUBBARD 740

On Entropy. W. S. FRANKLIN 766

The Effect of Pressure on the Aluminum Rectifier. A. P. CARMAN and G. J. BALZER 776

Proceedings of the American Physical Society 782

The Relation between Zero Shift and Size of Wire in the Moving Coil Galvanometer, *Walter P. White;* Neutral Contacts and Switches, *Walter P. White;* A Special Form of Surface Bolometer for Total Radiation Experiments, *E. F. Northrup;* Some Phosphorescent Salts of Sodium with Cadmium, *C. W. Waggoner;* The Effect of Temperature on the Ionization of a Gas, *J. H. Clo;* The Inductance of a Metal Tube Bent into the Form of a Circular Ring, *F. W. Grover;* A Test Object for Photometry by Visual Acuity, *Herbert E. Ives;* A Graphic Recorder for Cooling Curves, *C. B. Thwing*

Index 790

THE PHYSICAL REVIEW
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THE

PHYSICAL REVIEW.

STUDIES IN THERMO-LUMINESCENCE.

III. The Distribution of Energy in the Luminescence Spectrum of Sidot Blende.[1]

By C. A. Pierce.

Fluorescence at Room Temperature.

ABOUT two years ago an attempt was made by the author to study the energy distribution in spectra of fluorescent and phosphorescent powders by means of photographic methods. After a little success, the experiment was dropped due to the lack of a photographic plate sensitive over the region of fluorescence of the powder that was being experimented upon. At the beginning of the present college year, interest was again stimulated by the publication of an article by Ives and Coblentz, on the distribution of energy in the light of the firefly, in which the spectrum of the firefly's light was photographed. At about the same time, Professor E. L. Nichols suggested that Cramer's "trichromatic plates" might be sensitive to the portion of the spectrum included by the fluorescence light of Sidot blende. The plates were tried and proved to be suitable.

The method used in the study of the energy distribution consisted of photographing on the same plate one spectrum of the fluorescence light and four spectra of the light of an acetylene flame. Different intensities of acetylene were used for the four spectra, while the time

[1] The fluorescent powder that was used in these experiments was "Emanationspulver." The same sample of powder was used that had been used earlier in some experiments described in The Physical Review, Vol. XXVI., No. 4, April, 1908.

of exposure for the five spectra was the same. Knowing the distribution of energy in the acetylene flame,[1] the distribution in the fluorescence light was obtained by photometric comparisons of the spectra on the plate.

During this set of experiments the fluorescent powder was contained in a square dish made of platinum foil. The foil was connected to and supported by copper leads so that the temperature of the powder could be raised and controlled by passing electric current through the foil. The temperature was measured, if different from room temperature, by means of a copper-constantine thermo-couple placed in the midst of the powder. The blue lines of a mercury-arc lamp were used to excite the powder. The various intensities of acetylene light were obtained by screening off all but the center of an acetylene flame and moving the flame with the screen to different distances from the slab of magnesia which reflected the light into the slit of the spectrum camera. The camera consisted of a direct-vision spectroscope set so that the spectrum could be focused on a sensitive plate held in a plate holder.

The plates were handled and developed in complete darkness. The developer was freshly mixed from a stock solution and of a standard strength, and the length of development was timed, being for most of the plates eight minutes. The temperature was brought to 20° at the beginning of development and the plates were rocked mechanically during the development. The plates were fixed, at first, for thirty minutes, after washing in three separate waters, and the temperature of the fixing bath was brought to 20° at the beginning of the fixing. Later not so much care was used in the fixing because it was found to be inadvisable to intercompare spectra on different plates. After fixing, the plates were washed in running water for about thirty minutes, then thoroughly rubbed by hand and dried. Each plate was dried in such a position that the last portion to drain was a part upon which no measurements were to be made.

The distribution of denseness in any spectrum on a plate was obtained by pushing the plate past a brightly illuminated slit placed

[1] On the Distribution of Energy in the Visible Spectrum, by E. L. Nichols, PHYS. REV., Vol. XXI., p. 147, Sept., 1905.

squarely across the spectrum, and measuring the transmitted light by means of a Lummer-Brodhun photometer. The source of light to illuminate the slit and the standard light consisted of two carbon filament electric lamps with frosted bulbs. The light back of the plate was concentrated on the slit by a reflector. The current supplied to the lamps was held practically constant. It was found by actual test that a change of five volts was necessary to vary the relative intensities of the lamps enough to affect the settings of the photometer appreciably. The lamps were run at six per cent. above normal voltage to increase the candlepower and were lighted only long enough to make the measurements.

The wave-length measurements were made by calibrating in wave-lengths the screw which pushed the plate past the slit on the photometer bar. A zero wave-length was obtained on the plate by photographing the three blue lines of the mercury arc superimposed on the different spectra. These lines were in an entirely different region from that occupied by the spectrum of the fluorescence light. The calibration of the screw was made by photographing the entire visible spectrum of the mercury arc with the spectrum camera and setting one line after the other directly in front of the slit on the photometer bar. This slit was always opened just as wide as the width of the lines in the spectra and was placed parallel to these lines. The standard lamp was screened off by means of a variable slit so that the photometer could be used on whatever part of the bar that was desirable.

Fig. 41 shows the curves obtained by plotting the light transmitted through the spectra on one of the plates which had been exposed as described above. Each exposure was 60 minutes long and was made with the slit opened 40 units. Curves 1, 2, 3 and 4 represent the spectra of acetylene light at intensities 32, 16, 8 and 4 respectively. Curve 7 represents the spectrum of the fluorescence light. Curve 6 represents the distribution of energy in the acetylene flame and is assumed to correspond to curve 3. Then the energy curve corresponding to curve 2 will have ordinates equal to 16/8 times the corresponding ordinates of curve 6, etc. Wherever curve 7 crosses curve 3, the energy for that wave-length is represented by the ordinate on curve 6 for that wave-length. Wherever

curve 7 crosses curve 2, the energy for that wave-length is 16/8 times the ordinate of curve 6 for that wave-length, etc.

Since the curves intersect at only a few points, it is necessary to

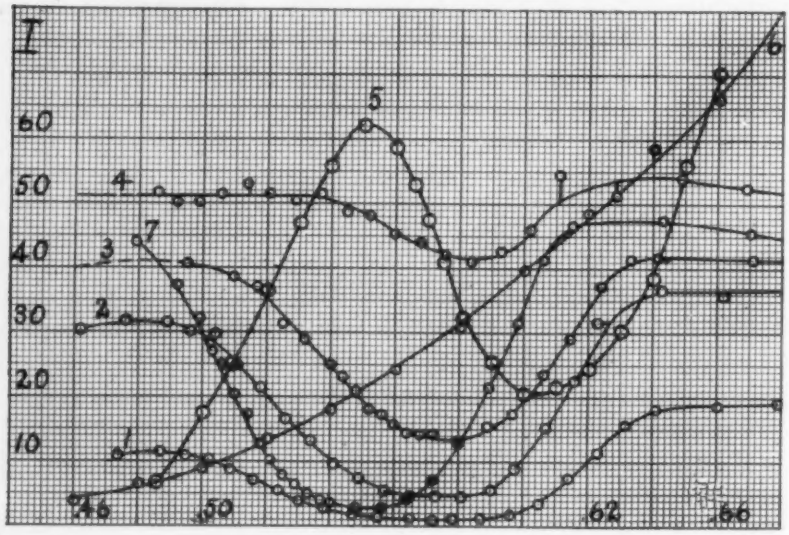


Fig. 41.

get other points on the desired energy curve by interpolation. This is done systematically and as follows: Suppose wave-length μ_1 is under consideration. A curve is plotted with the intensities of acetylene, 4, 8, 16 and 32, as abscissæ and the intersections of the vertical at μ_1 with the curves 1, 2, 3 and 4 as ordinates. From this curve is picked off the intensity of acetylene that would have coincided with curve 7 at wave-length μ_1. Fig. 42 shows six curves drawn in connection with Fig. 41. Curves 1, 2, 3, 4, 5 and 6 correspond to wave-lengths $\mu = 0.50$, 0.51, 0.52, 0.53, 0.54 and 0.55 respectively. The circle on each curve shows the point picked off.[1] On curve 6, Fig. 42, 23.5 is the abscissæ

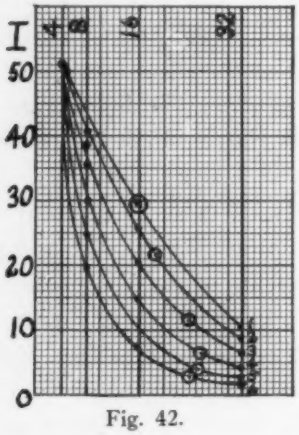


Fig. 42.

[1] The curves shown in this article do not exactly agree with the original curves from which the calculations were made due to inaccuracies in inking in the lines.

corresponding to 2.8, the ordinate on curve 7, Fig. 41, at $\mu = 0.55$. Hence the ordinate at $\mu = 0.55$ on curve 5, Fig. 41, which shows the distribution of energy of the fluorescence light is equal to 23.5/8 times 21.3, the ordinate on curve 6, Fig. 41, at $\mu = 0.55$.

Curve 5, Fig. 41, shows the energy curve of fluorescence as computed from the other curves in Fig. 41. The curve has a well-defined maximum at $\mu = 0.55$, a well-defined minimum between $\mu = 0.46$ and $\mu = 0.48$, and another minimum at $\mu = 0.60$. Later it will be seen that the shape of the curve for wave-lengths longer than $\mu = 0.60$ is uncertain.

Fig. 43 shows another set of curves corresponding to those in Fig. 41. The length of exposure was 30 minutes for each spectrum

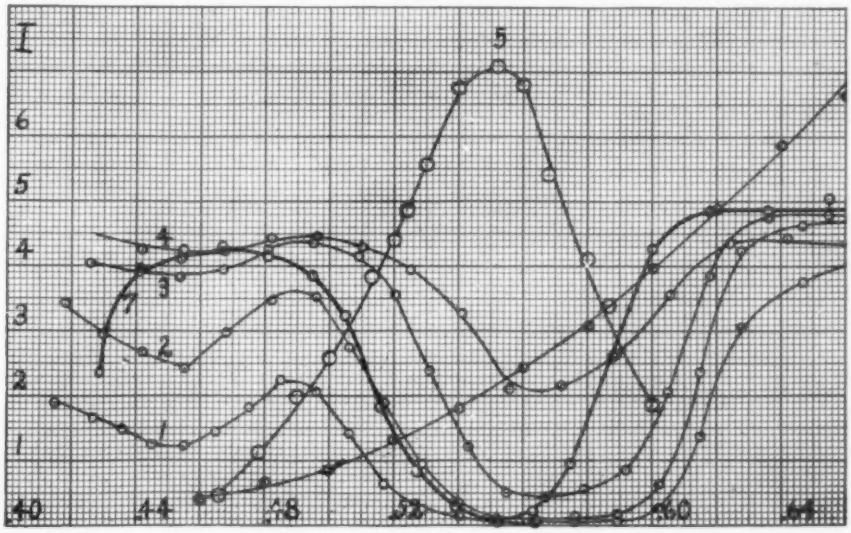


Fig. 43.

with a slit width of 20 units. The intensities of acetylene flame were 32, 20, 12 and 6 for curves 1, 2, 3 and 4 respectively. Curve 6 is assumed to represent the energy distribution in curve 4. Curve 5, which shows the distribution of energy in the fluorescence light, is similar to the corresponding curve 5, in Fig. 41. This shows that the curve is not materially influenced by two factors, length of exposure and width of slit in the spectroscope.

The Sidot blende was excited by the three blue lines of the

mercury-arc spectrum. While these lines are in a different region of the spectrum from that occupied by the fluorescence band, yet there was considerable halation shown on the plates about the three lines and the halation might extend far enough to change the shape of the curves in Figs. 41 and 43 in the region of smaller wave-lengths. To test this point, a set of curves were taken in which one curve represents the light of the three lines of the mercury arc reflected from a slab of magnesia, which was assumed to be as good a reflector as the Sidot blende. Fig. 44 shows the curves. Curves 1, 2, 3 and 4 correspond to different intensities of acetylene light

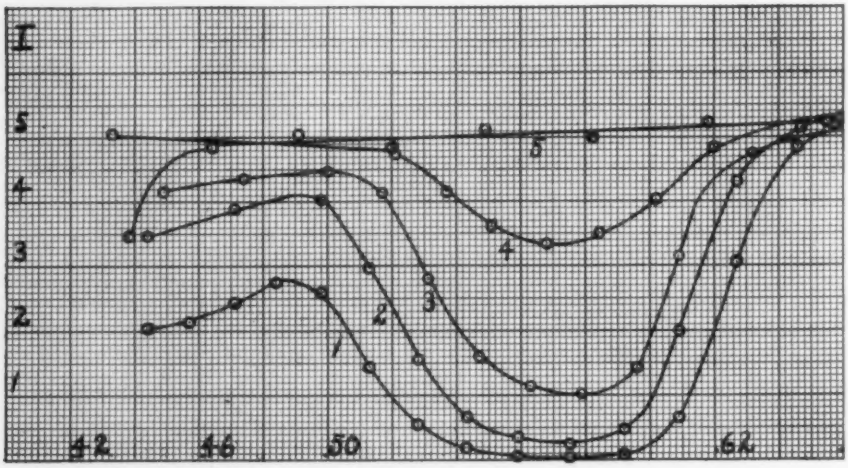


Fig. 44.

and 5 is the curve of reflected light. It is seen that halation of the mercury lines plays no important part for wave-lengths longer than $\mu = 0.46$, *i. e.*, no error is introduced in the curves marked 5 in Figs. 41 and 43. The slit opening in the spectroscope was 20 units and the length of exposure was 30 minutes in Fig. 44.

A set of curves, Fig. 45, was taken with the conditions so arranged that very intense negatives were obtained, in an endeavor to obtain the shape of the energy curve for wave-lengths longer than $\mu = 0.60$. The curves are marked similarly to those in the previous figures. Curve 5 shows the energy distribution of the fluorescence light. The maximum is shifted a little from $\mu = 0.55$

but otherwise it corresponds very well to curves 5 in Figs. 41 and 43. In Fig. 45, the data are inaccurate for computing curve 5 for wave-lengths greater than $\mu = 0.60$. Inspection of curve 4 shows that it crosses curves 1 and 2 in the region of longer wave-lengths. The same general departure is found in Fig. 43. This inaccuracy is probably due to a reversal in the negative though none is evident to the eye. It was found to be possible to take negatives which

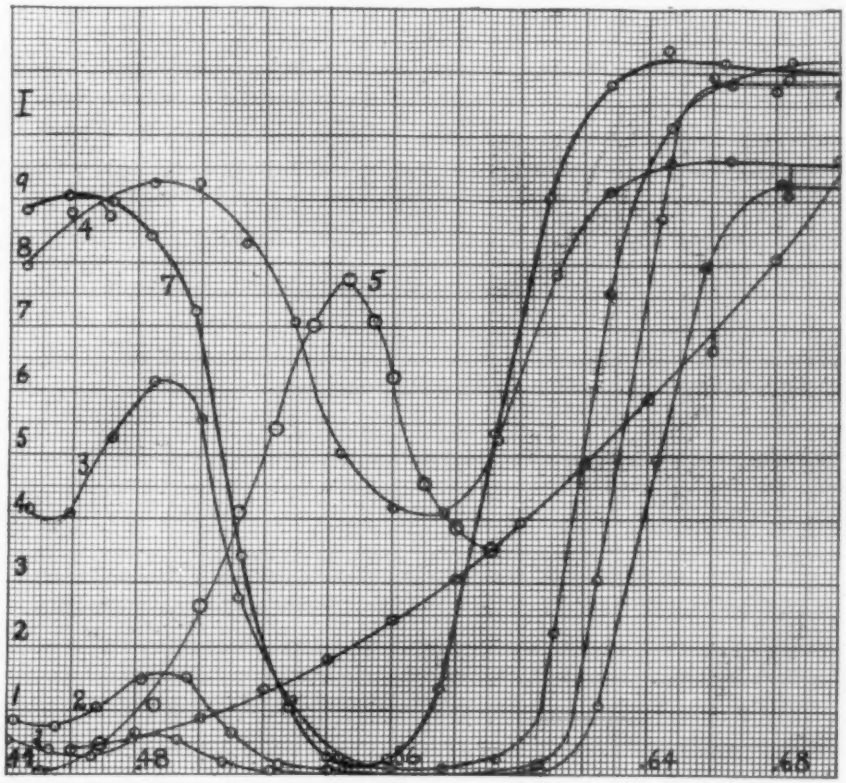


Fig. 45.

showed a decided reversal. The conditions were not found, however, under which a negative would surely show no reversal. If curves 3 and 4, Fig. 45, were where they apparently ought to be, with reference to curves 1 and 2, then curve 5 would rise for wave-lengths longer than $\mu = 0.60$, just as in Fig. 41. It is clear, as stated before, that no evidence is obtainable from these curves as

to the shape of the energy curve of the fluorescence light for wave-lengths greater than $\mu = 0.60$. Many more curves were taken than these shown, but no additional evidence was obtained, and the curves here reproduced are typical of all.

PHOSPHORESCENCE AT ROOM TEMPERATURE.

In order to obtain the distribution of energy in the phosphorescence light, it was necessary to add to the apparatus already described a shutter which would close the spectrum camera and excite the powder; then shut off the exciting light and open the camera. The shutter was operated by a constant speed motor. Levers, springs and triggers were so arranged that the shutter operated in a small part of a second. The length of excitation and decay could be increased or decreased together by changing the speed of the motor, while either the length of excitation or the length of decay could be varied alone by rearrangement of parts of the controlling devices. The total time of exposure of the photographic plate to the phosphorescence light was made equal to the length of exposure of the acetylene spectra.

With the apparatus described above, the photographic negative of phosphorescence was obtained by light which varied in intensity, for the phosphorescence decayed after the exciting light was closed off in the manner typical to phosphorescent powders. However, if an energy curve is obtained similar to that for fluorescence, it is nearly certain, not only that the energy curve does not change with decay but also that it does not change when the exciting light is shut off.

Fig. 46 shows the energy distribution in the phosphorescence light of Sidot blende. The powder was excited each time for $8\frac{3}{4}$ seconds and allowed to decay $10\frac{1}{8}$ seconds. The powder was not exposed to infra-red before each excitation. The effective length of exposure of the photographic plate was 60 minutes. Curves 1, 2, 3 and 4 show the transmitted light of the photographic spectra corresponding to intensities of acetylene equal to 6, 4, 2 and 1 respectively. Curve 5′ shows the transmitted light of the phosphorescence spectrum. Curve 5 shows the energy curve for the phosphorescence light.

It is seen that in general curve 5 corresponds to the similar curves for fluorescence light. That is, there is apparently no difference between fluorescence light and phosphorescence light immediately after excitation in the case of Sidot blende. Further experiments are needed to show whether any change occurs in the energy curve during decay and data for this are being obtained by the author at the present time.

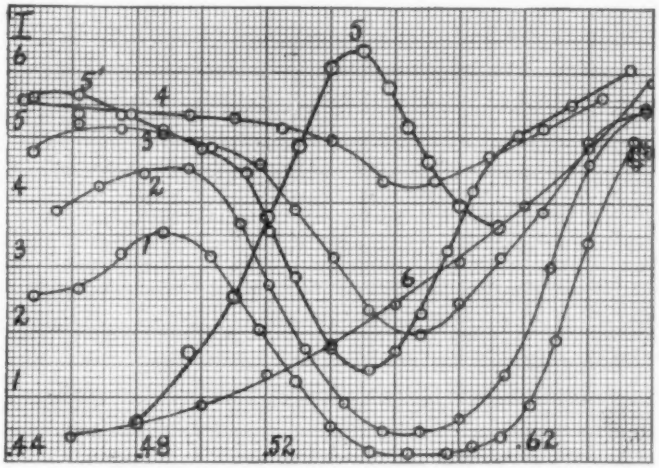


Fig. 46.

Discussion of Method and Results.

The chemical change made in a photographic plate depends upon the wave-length and intensity of the incident light and upon the length of exposure. If several spectra are photographed upon the same plate and the length of exposure is the same for all the spectra, then the denseness of the different negatives at any wave-length will depend only upon intensity of incident light at that wave-length, assuming a small opening of the slit to the spectroscope, uniform development, non-halation, etc. Since intensity is proportional to the rate at which energy is received from the source, the denseness of the different negatives at any wave-length depends upon the energy received from the source at that wave-length. By photographing several negatives of one source of light of known energy distribution at different distances from the spectroscope, curves

can be drawn showing the relation between energy received at any wave-length and denseness of negative. If a spectrum of another light of unknown energy distribution is photographed on the same plate, its energy distribution can be obtained by comparison of the denseness of its negative with the calibrated densities. The densities can be compared by means of the light transmitted through the negatives at different wave-lengths.

If the slit opening in the spectroscope is not very small, the denseness of the negative at any wave-length will not depend alone upon the energy received at that wave-length, but will also depend upon the energy received at wave-lengths differing but little from the wave-length in question. Consequently a small dimple in a curve might be obliterated by a wide slit opening. The effect of slit opening can be tested by using different openings, finally using the one which experience dictates.

The effect of halation is more troublesome than slit opening, and was present more or less in all of the negatives. The effect of halation is to broaden the band of energy distribution, but not to change the position of the maximum point of the band. It is believed that halation in the present experiments was not of sufficient effect to cause any serious error in the curves.

The plates were developed immediately after the exposures, which were made one directly after the other, so any error due to creeping of the chemical reactions in the film was eliminated as far as possible.

The photographic measurements were difficult to make due to the large differences in amount of light transmitted in different parts of the negatives. At the beginning of the experiments, four settings of the photometer were made for each point measured. Later two settings were found to be sufficient, one approaching uniformity of illumination from each direction. The average of the two values calculated from the two settings was taken as the true ratio of standard and transmitted lights. Remeasurement of a set of curves never proved any exceptional accuracy, but always gave the same type of energy curve with the maximum at about the same wave-length. Consequently the measurements can be said to be substantiately correct.

The results of these experiments show that the energy curve of

the fluorescence light of Sidot blende consists of a band extending from about $\mu = 0.46$ to $\mu = 0.60$, having a maximum at $\mu = 0.55$. There may be another band situated in the region of longer wave-lengths. Furthermore, the energy distribution in the fluorescence light and the phosphorescence light immediately after excitation is the same.

Further experiments are now being carried on by the writer to find whether any change in the energy curve takes place during decay, or is brought about by the influence of infra-red rays or by other means.

PHYSICAL LABORATORY, CORNELL UNIVERSITY,
March 21, 1910.

ON THE EXTRA TRANSMISSION OF ELECTRIC WAVES.[1]

BY F. C. BLAKE.

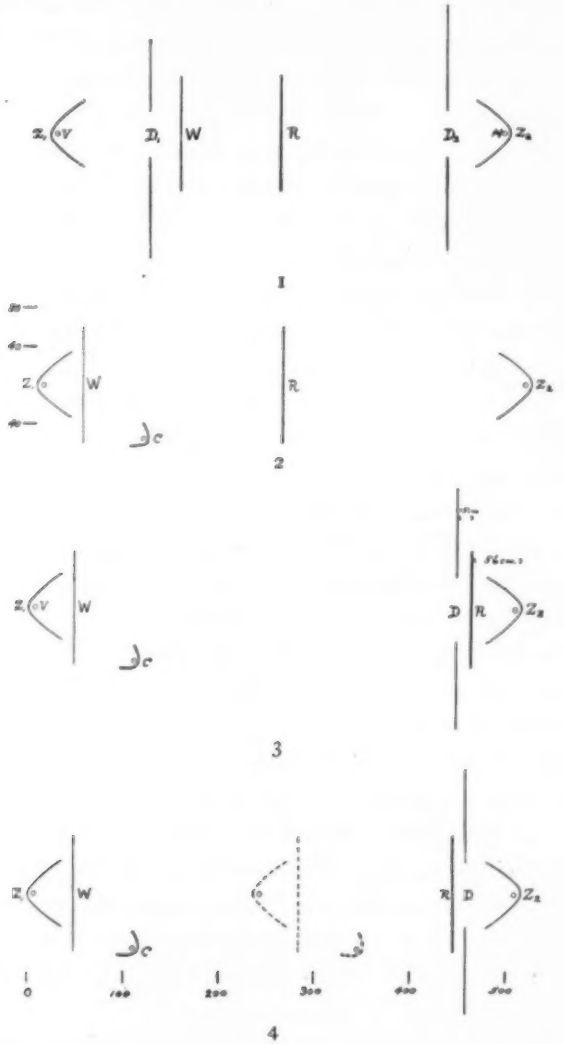
IN the May number of the PHYSICAL REVIEW of 1907 appeared a criticism by Dr. Clemens Schaefer[2] of the work of Blake and Fountain[3] on the transmission of electric waves through resonator gratings. Dr. Schaefer takes these authors to task for overlooking an important article by him,[4] and with good right. On behalf of Dr. Fountain and myself I here express regret that this oversight occurred and cheerfully acknowledge any priority that Dr. Schaefer's article contains.[5]

Before replying to Mr. Schaefer, I wanted to perform some experiments, and it is only lately that I have been able to complete them. In one part of his criticism, he claims to have repeated some of our experiments, the only change he made being the insertion of two diaphragms. With this change he was unable to verify our results on extra transmission. I felt that the use of diaphragms was unwarranted on the ground of the enormity of the diffraction effects thereby introduced, but it plainly was a question for further experimentation to decide, hence the delay in my reply.

It seems best before taking up the various points in Schaefer's criticism, to describe the new experiments I have performed bearing upon the phenomenon of extra transmission. The apparatus used was identical with that used in the previous work,[6] with the exception of the resonator grating and its supporting framework. Columbia University kindly donated the parabolic mirrors, the vibrator

[1] Read before Section B, A. A. A. S., December, 1908.
[2] PHYS. REV., XXIV., p. 421, 1907.
[3] PHYS. REV., XXIII., p. 257, 1906.
[4] Ann. d. Phys., Vol. 16, p. 106, 1905.
[5] By letter at the time I made such acknowledgment.
[6] Blake and Fountain, loc. cit.

and the receivers and I herewith express my best thanks to Professor Hallock and the department of physics there. The arrangement of apparatus is shown in Figs. 1–4, drawn to scale. Z_1, Z_2 are the



1 2 3 4

Figs. 1–4.

zinc mirrors, D_1 and D_2 are diaphragms of galvanized iron of variable aperture, W is a rectangular wire grid 120 cm. on a side, with the distance between the wires 2.5 mm. The wires, No. 36 B. & S.,

were strung vertically, at right angles to the electric force of the oncoming wave. This grid was used to make sure that the wave was plane-polarized, although I am convinced as before[1] that its use is unnecessary provided one is careful that the axes of vibrator and receiver are in the focal lines of their respective mirrors. C and M are the check and main receivers and V the vibrator. R is the resonator grating—a sheet of plate glass 122 × 96.5 cm. carrying tin-foil strips whose distribution was varied. Instead of R, a bare sheet of plate glass B could be inserted at will. The average thickness of the bare glass was 7.3 mm., that of the resonator glass 6.8 mm., a difference sufficiently great to make the ratio R/B for transmission, with both glasses bare 1.022, obtained by a long series of alternate readings. In all the curves and results of this paper this ratio has been taken into account.

One of the galvanometers used was a du Bois-Rubens type, the other a Broca instrument. They were given the same period and were interchanged in the receiver circuits whenever it was desirable. The former had a sensitiveness roughly of 2.5×10^{-9}, the latter, 10^{-8}, for a period of 4 seconds. The period was varied from time to time, according to the energy available, the time for a complete swing being varied from 4 to 6.5 seconds.

Since Schaefer had insisted upon the use of diaphragms in such work on electric waves, the first thing I did was to introduce two such diaphragms each 8 ft. 6 in. square, using a resonator system identical with Table I., Fig. 9, Blake and Fountain, except that the resonators were 5 instead of 6 cm. long. Fig. 5 shows the results obtained. It was found impossible under the working conditions at first obtainable to get sufficient energy through two apertures 32 cm. vertical by 24 cm. horizontal to make the results trustworthy, so apertures 47 × 38 were chosen. The points shown are the mean of two sets of readings taken thus: $ARBRBRA$ (A = air = free radiation, R = resonator glass, B = bare glass). These apertures fulfill the condition imposed by Schaefer, that they be smaller than the mirror apertures, 68.8 × 60.5 cm.[2] Larger aper-

[1] Blake and Fountain, loc. cit., p. 266.

[2] Apparently the figures 70 × 63 cm. given on page 259, Blake and Fountain, are slightly too large. This error in measurement is of course unimportant.

tures were then used and finally both diaphragms were removed. Extra transmission is plainly present in all cases. It is affected, though not seriously, by the size of the diaphragm apertures. It should be noted that the energy at the main receiver was greater for the apertures 70 × 60 than for the diaphragms wholly removed. This point will be discussed later.

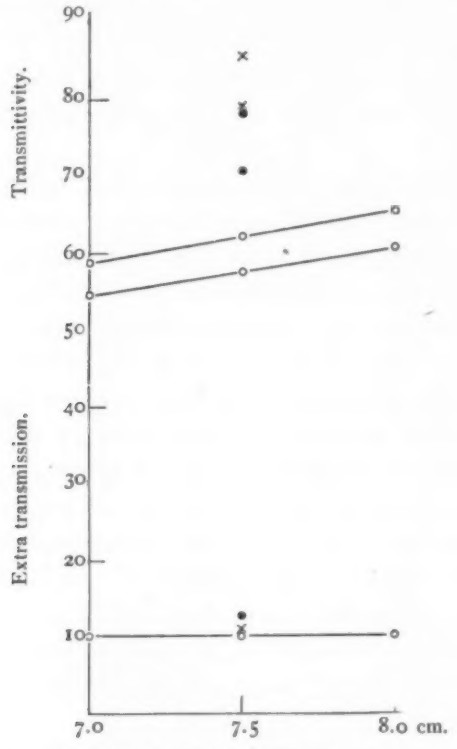


Fig. 5. Resonator grating, 13 columns of 39 each. Length of resonator, 5 cm.; width 0.2 cm. Distance between resonators, side-on, 2.8 cm., end-on, 1 cm. For the points marked by crosses the apertures D_1 and D_2 were 68.8 cm. × 60.5 cm.; circles, 47 × 38 cm.; dots, both diaphragms removed.

Schaefer explains extra transmission on the ground of the divergent properties of the waves employed by us, although he doesn't state why the waves sent out by a vibrator and collected by a receiver each of which is placed accurately within 0.5 mm. in the focal line of a parabolic mirror of 7.5 cm. focus should be divergent.

I cannot conclude by a study of his criticism that he refers to the well-known divergent property of electric waves in a direction parallel to the focal line of the parabolic mirrors. This latter property will also be discussed later. To test this explanation the vibrator was purposely moved from the focal line in both directions, the main receiver being left undisturbed at 7.5 cm. With apertures 47×38, the transmittivity for each glass separately (*i. e.*, the ratio between the energy at the main receiver through each glass compared to that through air) was increased in going from a divergent to a convergent wave but the extra transmission remained constant (Fig. 5).

It is well known that a vibrator formed of spherical balls shows greater irregularity in its action after a few readings than one having flat parallel surfaces at the spark gap. Accordingly a vibrator was made by boring the two $\frac{3}{8}$-inch balls and inserting steel cylinders, threaded and slightly conical, and projecting beyond the brass about one millimeter. The area of each of the cylinders at the spark gap was roughly 0.2 sq. mm. It was assumed that the length of the wave emitted by such a vibrator was not materially changed from 10 cm., but as I couldn't be sure of this it was thought better to replace the resonator system by a system consisting of strips 90 cm. long by 0.2 cm. wide, with a side-on distance of 2.8 cm.[1] Such a distribution should be independent of small variations in the wave-length. Moreover, it had been found[2] to give a larger extra transmission than that given by a system of double the resonance-length. Throughout the rest of this paper this latter system was used.

The results obtained with such a system are shown in Fig. 6. The arrangement of apparatus is shown in dotted outline in the figure, the location of the resonator system being varied between the diaphragms. The apertures 32×24 allowed so little energy to pass through that for them it was thought better to lay more stress on the extra transmission than on the transmittivity. Accordingly twenty-five readings were taken alternately thus: *BR-*

[1] The side-on distance used by Blake and Fountain was 2.8 cm., not 3.0 cm. as Dr. Schaefer understood. This would of course affect his arguments not at all.

[2] See Fig. 11, Blake and Fountain, page 273.

BRBRB, etc., for each of the points shown. To obtain an idea of the constancy of the readings and of the accuracy of the work the figures are given for the position of the resonator system nearest the main receiver. Ratio M/C for *B's*, 1.152, 1.168, 1.175, 1.089, 1.145, 1.147, 1.158, 1.121, 1.137, 1.112, 1.093, 1.118, 1.130. Ratio M/C for *R's*, 1.226, 1.229, 1.237, 1.187, 1.256, 1.262, 1.258, 1.274,

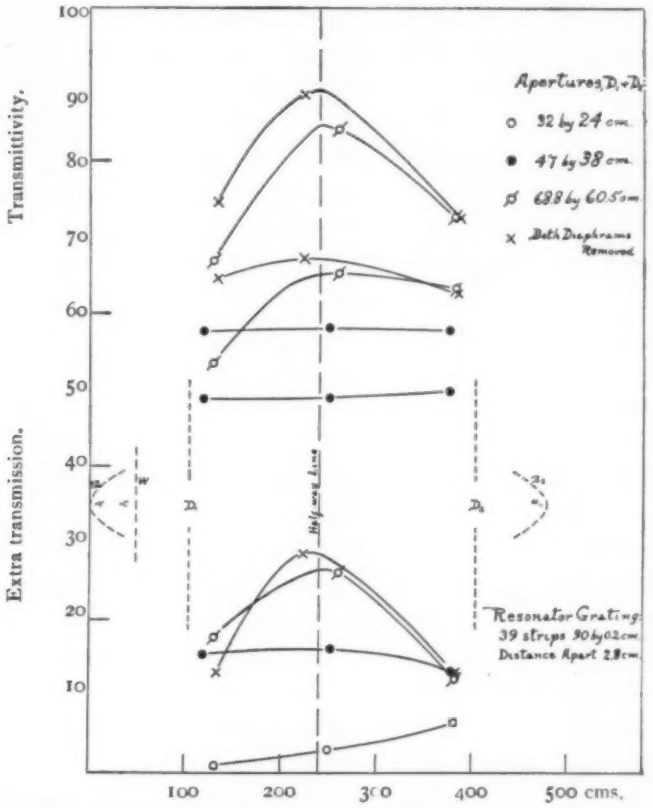


Fig. 6. In the curves in the upper part of the figure the lower curve of each pair refers to bare glass, the upper curve to the resonator glass.

1.208, 1.211, 1.226, 1.229. Mean R, 1.234; mean B, 1.134. R/B = 1.088; extra transmission reduced, 6.5 per cent. For apertures 47 × 38, the extra transmission as well as the transmittivity seemed more or less independent of the location of the resonator system. For apertures the size of those of the parabolic mirrors the extra transmission was larger when the resonator system was near the

position half-way between vibrator and main receiver than for either of the two other positions. This increase in the extra transmission in the mean position was augmented when the diaphragms were removed, and so a more careful study was made of it. It should be noted from Fig. 6 how, for apertures 47 × 38 or larger, the extra transmission was practically constant at 13 per cent. for

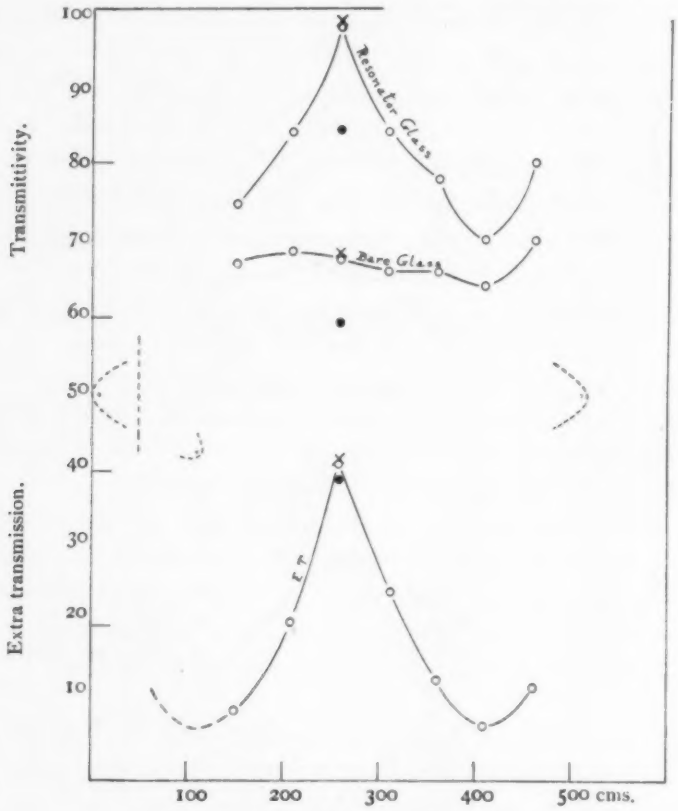


Fig. 7. Both diaphragms removed.

the positions of the resonator system nearest the main receiver. The fact that for apertures 68.8 × 60.5 cm. the transmittivity for the bare glass was a function of the location of the resonator system with respect to the diaphragms points to diffraction effects around the glass. I think that these diffraction effects, as will be seen later, occur around those edges of the glass which are at right angles to the electric force.

After changing the location of the check receiver to the position shown in Fig. 2 and in dotted outline in Fig. 7, the curves of Fig. 7 were taken with both diaphragms removed. These curves were taken before the great importance of *extremely* accurate adjustment was realized for this position of the resonator system half-way between the two parabolic reflectors. Each point of the curves was determined from the following series, *AARBRBRBRAA*, and so could not be much in error. However, the extra transmission curve of Fig. 7 shows the half-way position to be a critical one, one where it is very necessary when diaphragms are not used to have the straight line joining the vibrator and main receiver accurately divide the 90 cm. of the strip lengths into two equal parts. To illustrate, the points (circles o) of Fig. 7 having been taken with the resonator grating of 39 strips the top eight and the lower eight strips were removed, leaving 23 strips extending over 66.2 cm. space in a vertical direction, so that in a direction at right angles to the electric force the resonator grating was now smaller than the aperture (68.8 cm.) of the parabolic mirrors. With no great care being used in pushing the resonator plate into the path of the wave the black circles of Fig. 7 were obtained. A sideward adjustment of 2.3 cm. (determined by the use of plumb-lines at the centers of the vibrator, resonator-plate and main-receiver) gave the crosses shown in the figure. Repetition of the adjustment and non-adjustment confirmed this. To show clearly the need for this adjustment the actual figures are given in Table I. Fig. 7 shows clearly that when the proper care was used to have the straight line connecting the vibrator and main receiver pass through the center of the resonator system, the transmittivity was unaffected by the removal of the eight strips that extended above and below the apertures of the parabolic mirrors. Indeed, although without this adjustment the transmittivity for both the resonator and the bare glass is affected, the extra transmission is but slightly changed.

I can not ascertain from Schaefer's discussion of our experimental arrangements whether in his criticism of the resonator system's having a larger area than the aperture of the parabolic reflectors his objection refers so much (if at all) to the direction parallel to the focal line as to the direction at right angles to such line. If one

TABLE I.

Imperfect Adjustment (Displaced 2.3 cm.).					Plumb-line Adjustment.				
Medium Inserted.	Ratio *M/C.*	Means.	Ratios (Per Cent.).	Extra Transmission (Reduced).	Medium Inserted.	Ratio *M/C.*	Means.	Ratios (Per Cent.).	Extra Transmission (Reduced).
A	1.243	*A*1.238			*A*	1.234	*A*1.248		
A	1.213		*R/A*		*A*	1.261		*R/A*	
R	1.062		84.2		*R*	1.214		98.4	
B	0.748	*R*1.042			*B*	0.853	R1.227		
R	1.030		*B/A*		*R*	1.237		*B/A*	
B	0.719		59.4		*B*	0.846		68.2	
R	1.030	*B*0.735			*R*	1.229	*B*0.850		
B	0.738		*R/B*		*B*	0.850		*R/B*	
R	1.045		141.8	38.8 per	*R*	1.227		144.4	41.3 per
A	1.246			cent.	*A*	1.230			cent.
A	1.248				*A*	1.267			

is to limit the resonator system in the former direction to dimensions less than the mirror apertures in this direction it becomes at once important to ask oneself to what extent this dimension of the parabolic mirrors plays a part in his experiments. In other words, if the focal line be thought of as limited in its length by the two parallel bounding planes of the parabolic mirrors, what, expressed in wave-lengths, should be its length. The question is a fair one and has, so far as I know, never been investigated in electric-wave work. Although I think it is of some importance, yet I do not believe Schaefer had it in mind in expressing his objections. If he did, he might well have asked himself ought not he and Aschkinass and all the other investigators in this field to have employed paraboloidal rather than cylindrically parabolic mirrors?

The importance of side-adjustment was investigated more fully in Fig. 8. With the same distances and apparatus as in Fig. 7 (except that the bare glass alone was used) the central position was carefully determined by the use of plumb-lines in the manner already described. To eliminate vibrator-deterioration this central position was used as a check position after determining any two successive points of curve *B*, Fig. 8. The energy at the main receiver through the bare glass in the central position was chosen as 100. When the bare glass plate was 27 cm. out of center enough energy got around it by free radiation to give 100 at the main receiver again. The

slope of curve B at the central position toward either side shows the need for accurate adjustment. Then the apparatus was changed to an exact duplication of the arrangement employed by Blake and Fountain for transmission (*l. c.*, Fig. 4). Employing the resonator glass alone a similar curve, R, Fig. 8, was obtained. However, it has far less slope than B, showing the smaller need for accurate side-adjustment as the resonator system is moved from the position half-way between the parabolic mirrors. Then although the vi-

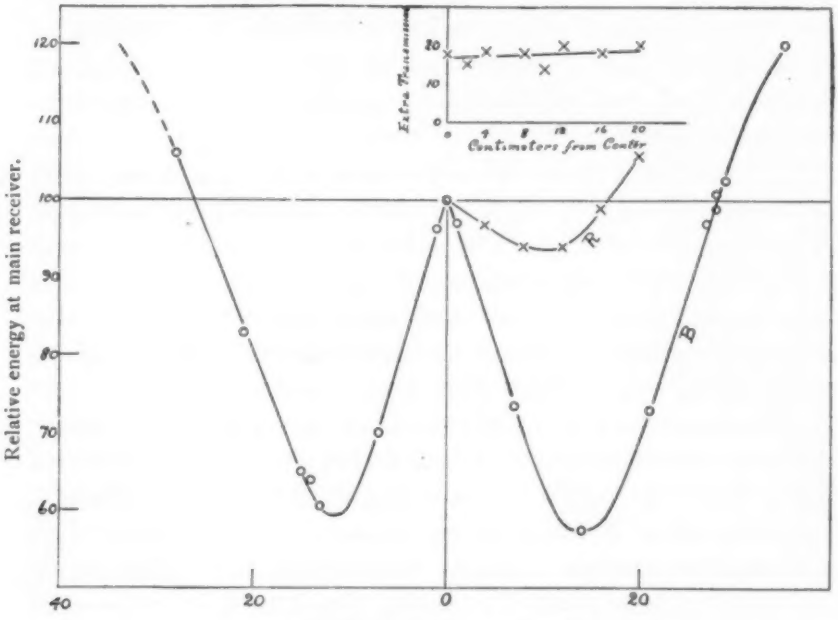


Fig. 8.

brator was pretty well worn and only a few readings were taken it was thought worth while to see to what extent the extra transmission was affected in the latter position by any lack of side-adjustment. Curve ET, Fig. 8, shows that it is practically unaffected, just as curve ET, Fig. 7, does for the half-way position. The transmittivity curves of Fig. 7 are subject to some correction due to lack of plumb-line side-adjustment. However, as I have just shown, curve ET of the same figure is free from this objection

largely, since care was always used to have the bare glass plate duplicate *exactly* the position of the resonator plate in taking a set of alternate readings. The minimum point at 408 cm. in curve *ET* is undoubtedly present. At the half-way position the extra transmission is a maximum and is seen to be a very large effect, so large that for 23 strips 90 cm. long and 2.8 cm. apart the resonator glass comes within 2 per cent. of giving the full free radiation energy at the main receiver! Undoubtedly diffraction effects play some part at the main receiver and it is very probable that the amount of diffracted energy as well as its phase is a function of the index of refraction of the intervening obstacle. If this is so it is not easy if at all possible to separate diffraction and extra transmission phenomena.

Since, as Fig. 7 shows, the extra transmission is so large in the half-way position, the cause for this is naturally to be sought. The phenomenon may be said to be a sort of *lens action* of the resonator system. The front of the wave as it strikes the resonator system may be taken as cylindrical approximately, with the generating line of the cylinder at right angles to the tin-foil strips. Thus the plane system of long strips takes these cylindrical waves and converges them, still kept cylindrical, upon the main receiver mirror just as a cylindrical lens converges the waves from a line source of light. As I have said I cannot determine from Dr. Schaefer's criticism that it is *this* divergent property of electric waves from cylindrically parabolic reflectors that he refers to. Moreover, if this property be an error it is an error that is common to the work of all the previous investigators. For I doubt if Dr. Schaefer is able to tell us what the width of an aperture in a screen should be in a direction parallel to the vibrator axis to eliminate this property. For instance, had the focal line of each of my parabolic mirrors been 100 cm. in length, and thereby for the arrangement represented in Fig. 7 the condition imposed by Schaefer being fulfilled that the resonator system be smaller in area than the mirror apertures, I believe the curves of Fig. 7 would not have been materially changed.

If the *lens-action* of the resonator system is the proper explanation for this very large increase in the extra transmission when vibrator

and receiver are equally distant from the system, I see no reason why this lens-action should not be present if one were to employ resonator strips in air instead of on glass. I mean to test this point as soon as may be feasible and to see how, starting with long strips, the lens-action if present is affected by successive shortenings of the strips. Probably there is a certain angle formed by the line joining vibrator to receiver and the line joining vibrator to either end of that particular strip in the same horizontal plane as the vibrator, where the effect is a maximum.

On account of the wave-front being cylindrical in form and the lens action of the resonator grating being thus for certain positions of the grating superimposed upon the true effect of extra transmission it seemed best to place the resonator grating as near as possible to the main receiver and by means of a single diaphragm of aperture 68.5 × 16 cm. to allow so small a portion of the wave-front through (except for diffraction effects due to the presence of the diaphragm) that the transmitted portion could be said to be plane in both directions of the aperture. This being done as shown in Fig. 3, the effect of changing the vibrator from its normal position was tried. In this work the usual series *AARBRBRBRAA* was taken for each position of the vibrator. Fig. 9 (circles o) shows the results. The extra transmission was about twelve per cent. (the vibrator was made of spherical balls without points) and was slightly larger for a convergent wave than for a divergent one. Then the effect of changing the width of the aperture was tried. Fig. 9 (crosses ×) gives the results. The extra transmission was constant at 11 per cent. though the transmittivity of both glasses varied. The relative energy at the main receiver for this last case as the width of the aperture was varied is plotted in curve *B*, Fig. 10. This curve is a free radiation curve through air, the energy at the main receiver for a width of aperture 32 cm. being taken as 100. The interposition of either the bare or resonator glass changed the character of the curve only for the larger apertures (see curve *B'* — here of course the energy through the bare or resonator glass for diaphragm aperture 32 was taken as 100). This curve was plotted incidentally from the results obtained from Fig. 9 (crosses ×) and as only four points were taken its character was not wholly deter-

mined. The fact that for an aperture 61 cm. the energy at the main receiver was only 77 per cent. of that for an aperture 32 cm. showed the presence of diffraction effects, as was to be expected. Other diffraction curves are shown in curves A and C, Fig. 10, A being taken with a diaphragm placed 15 cm. in front of the resonator position, Fig. 2. C was taken as shown in Fig. 4 in dotted outline. For all three curves of Fig. 10 the length of aperture was

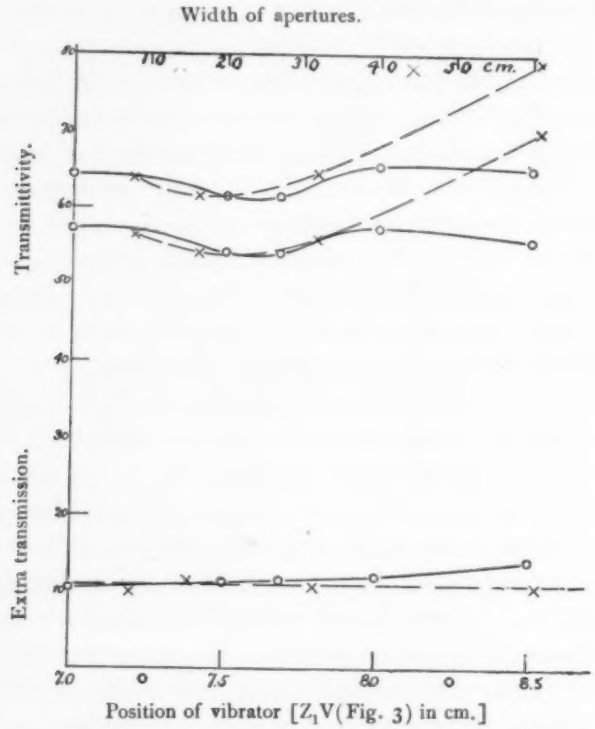


Fig. 9. For arrangement of apparatus see Fig. 3. Length (vertical) of aperture, 68.5 cm.

68.5 cm., the width alone being varied. C shows a diffraction maximum at 39 cm. and A at 63 cm.

Now theory shows[1] that if a is the distance of the vibrator and b that of the main receiver from the screen and ∂ the width of aperture then maxima occur when

$$\frac{\partial^2}{2\lambda}\frac{a+b}{ab} = \tfrac{3}{2} + 4h$$

[1] See, for example, Winkelmann's Handbuch der Physik, 2d edition, Vol. 6, p. 1060.

and minima when

$$\frac{\delta^2}{2\lambda}\frac{a+b}{ab} = \tfrac{7}{2} + 4h,$$

where h is a whole number. Of course both a and b are to have 15 cm. (twice the focal distance) added to them. Doing this and making $h = 0$, the figures for curve A are $a = 250$ cm., $b = 280$ cm., $\lambda = 10$ cm., whence $\delta_{\text{max.}} = 62.9$ cm., $\delta_{\text{min.}} = 96.1$ cm. For curve

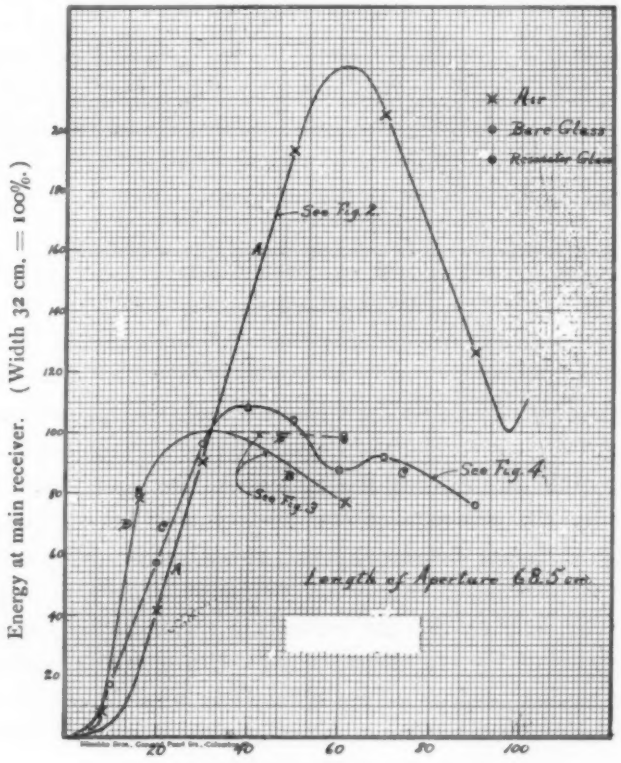


Fig. 10.

C, $a = 231$ cm., $b = 64$ cm. and $\delta_{\text{max.}} = 38.8$ cm., $\delta_{\text{min.}} = 59.2$ cm. There is thus for the maxima entire agreement between theory and experiment. Making the same calculation for curve B with $a = 451$, $b = 79$, $\delta_{\text{max.}}$ comes out 44.9 and $\delta_{\text{min.}} = 68.6$ cm. The maximum for B could easily be at 44.9 instead of at 32 as

shown, since no points between 32 and 61 were determined. For *A* and *B* the minima are not yet reached in the curves. For *C* the theoretical minimum at 59.2 cm., though small, plainly shows itself. For *A* I have extrapolated the minimum at 96 cm.

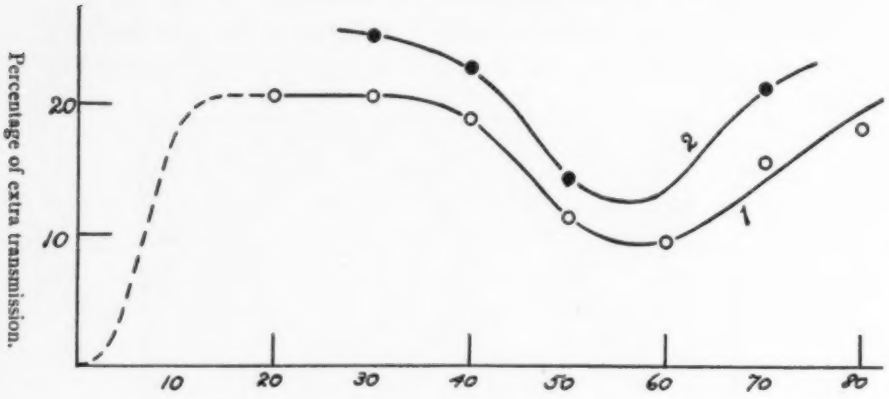


Fig. 11.

These curves of Fig. 10 show how strongly diffraction effects are present at the main receiver when a diaphragm is employed. Moreover, curve *B'* shows that the amount of diffracted energy is influenced by the presence of the resonator or bare glass, and in general in different degrees by the two glasses. Vice versa, the presence of diffracted energy influences in different degrees the energy that reaches the main receiver through the two glasses, as the curves of Fig. 11 clearly show. Curve 1 was taken with a vibrator having conical points about one mm. long, the parallel faces of the points having a cross-section of about 0.2 sq. mm. Each point on the curve was determined as the mean of the following series, *RBRBRBRBR*, and vibrator irregularity was eliminated by increasing the width of aperture by successive steps to the maximum width and then returning successively by steps to the minimum width. Relative distances for the apparatus are shown in Fig. 4 (vibrator mirror dotted), and plumb-line adjustment was used throughout. Curve 2 was taken under identical conditions except that the vibrator had 3 mm. points. The extra

transmission is greater for the 3 mm. vibrator than for the 1 mm. vibrator, to be explained probably by the change in the length of the wave emitted. Fig. 11 shows plainly the influence of diffraction on extra transmission. Curve *C*, Fig. 10, is the diffraction curve obtained from the measurements taken for curve 1, Fig. 11. It is very significant that the minimum extra transmission occurs at 59 cm., the exact location of the diffraction band in curve *C*, Fig. 10. Weak though this band is, it has a very large effect on extra transmission.

If, then, diaphragms are to be employed what should be their aperture width? A study of the curves of Fig. 10 shows that, in order to be as free as possible from the influence of diffraction, an aperture width should be chosen which falls on the first straight line part of that diffraction curve which corresponds to the momentary arrangement of apparatus. Naturally, one would choose if possible the width such that the energy would be equal to that corresponding to the entire absence of diffraction bands. For instance in Fig. 10, curve *A*, the ordinate for minimum is 100, for maximum 220. This makes the ordinate corresponding to the asymptotic point of Cornu's spiral 151, thus approximately giving for the diffractionless width of aperture 42 cm. But this width for another arrangement of apparatus may not be justifiable at all (*e. g.*, that for curve *C*). On such reasoning one is permitted from curve *C*, Fig. 10, and hence in Fig. 11 to choose width 30 cm. Thus for a vibrator having 1 mm. points the true extra transmission is 20 per cent., for a 3 mm. vibrator 25 per cent. For a spherical ball vibrator without points the true extra transmission was not obtained in the way indicated above, but judging from the results of Fig. 9 it is distinctly smaller, say 12 per cent. Now the curves of Fig. 10 were taken with a 1 mm. point vibrator and the diffraction bands were calculated for $\lambda = 10$ cm., the wave-length determined by Blake and Fountain for a spherical ball vibrator; moreover, the observed and calculated diffraction bands were found to agree exactly. And yet the point vibrator gives greater extra transmission than the spherical ball vibrator of the same wave-length. Possibly the point vibrator throws a larger per cent. of its radiated energy into the equatorial region than does the spherical ball vi-

brator and hence the greater extra transmission. It is to be borne in mind, of course, that these values for the true extra transmission are given as correct only for the particular resonator system used in this paper. Fig. 11, curve 1, shows the same extra transmission for width 20 as for width 30 cm. It would seem that for smaller widths the extra transmission remains constant at 20 per cent. so long as one remains on the straight line part of the diffraction curve, *i. e.*, down to 13 cm. width. Below that it probably bends rapidly toward zero. I have thus extrapolated the curve in Fig. 11.

Keeping the width of aperture constant at 40 cm. I then tried to see the effect on extra transmission of moving the vibrator away from the resonator system. In doing this the relative distance between vibrator and check receiver was kept constant. Here to eliminate vibrator irregularity the vibrator was moved away and then nearer again by successive steps. The usual series of nine alternate readings were taken for each position. Fig. 12, curve 1, shows the extra transmission curve, the energy curve being curve 2. The sinusoidal nature of curve 1 is very marked, and I thought it could be explained by giving successive values to h in the diffraction formulæ above. But I haven't been able to make the figures fit the formulæ. However, it should be remembered that the diffraction system is a compound system consisting of the resonator or bare glass and the diaphragm.

From the first it was thought that in general the use of diaphragms was not justifiable and so with the arrangement of apparatus shown in Fig. 3, the following variation was tried. Diaphragm aperture 47 × 38 cm., extra transmission 17 per cent.; aperture 32 × 24 cm., extra transmission 9 per cent.; relative energy at main receiver, 3 to 1. Then a second screen was inserted 120 cm. in front of vibrator, aperture 32 × 24 cm. for both screens. Extra transmission 5 per cent.; relative energy at main receiver for one screen (the one near the receiver) as compared with that for two screens, 3 to 1. Thus one ninth as much energy gets to the main receiver with two screens of aperture 32 × 24 as with one of aperture 47 × 38. Moreover, the second screen cuts the extra transmission almost in two. All this shows, it seems to me, that the relative energy diffracted out into regions other than the main direction of

the wave is much larger for the smaller aperture than for the large one, and hence the extra transmission is cut down. Each new aperture radically changes the character of the wave-front, diverting more and more of the energy from the equatorial path and the amount diverted would be affected differently by the resonator

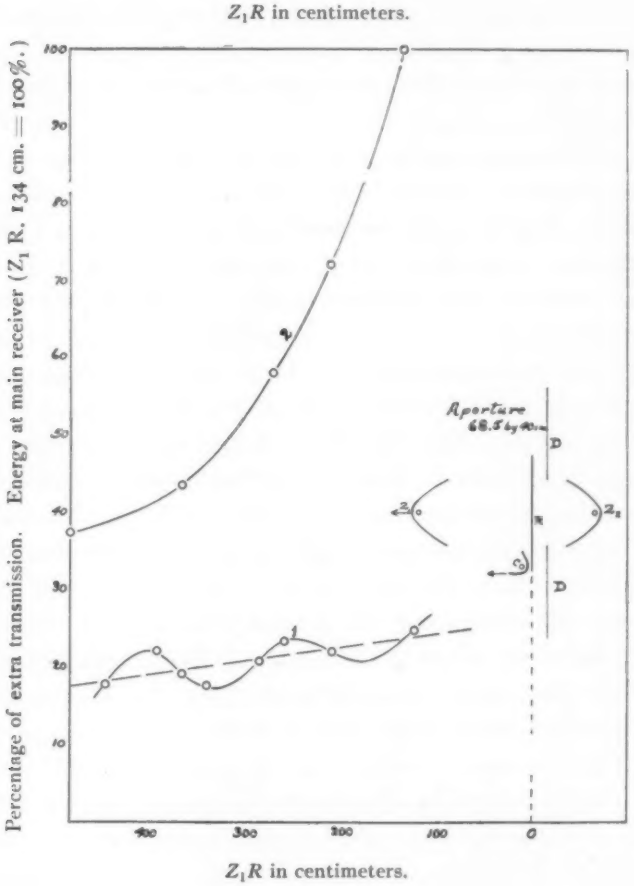


Fig. 12.

and bare glasses, hence the lowering of the extra transmission by using a second screen. Moreover, changing the length of the gap ought to introduce diffraction bands just as changing the width has been seen to do.

I contend, after these experiments, that in general in electric wave work of the sort here described, the use of diaphragms is *not justifiable.* The employment of two diaphragms is *never* justified, and if a single one is used, it should be placed as near to the main receiver mirror as possible and the width of its aperture should be such that diffraction bands are entirely absent at the receiver. If one uses cylindrically parabolic mirrors, the aperture *length*, should in my opinion, be at least equal to the height of the mirror aperture, although a small change of the length either way is probably immaterial. I have already explained how, in the most crucial position of the resonator system (the half-way position, Fig. 7) it was immaterial whether one employed a resonator system whose *length* was greater than or equal to the height of the mirror apertures. Doubtless the effect measured at the main receiver is dependent upon the *width* of the resonator system and its relative distance from the receiver. But so long as cylindrically parabolic mirrors are employed I see no criterion by which one may determine what the proper width of the resonator system is to be. To my mind it is meaningless to say that the width should be less than the width (dimension parallel to the focal line) of the parabolic mirrors.

In my opinion, for transmission work in electric waves it is far safer to employ no diaphragms but to have the transmission system as near as possible to the main receiver mirror and of such a *width* that it may properly be said to be infinite, thus preventing diffraction past the edges affecting the receiver. This could best be done by having the system practically touching the mirror and yet having the parabolic mirrors shallow.

Dr. Schaefer's objections consisted of two. He denied the existence of the phenomenon of extra transmission because he could not find it when he used diaphragms. And for good reasons. The apertures he employed were too small. The effect was there to the extent of 5 per cent. even with his arrangement, though it was not surprising he didn't find it. Had he studied the effect of the size of aperture he might have seen where the trouble lay. Nor is it surprising that Aschkinass and Schaefer[1] didn't find the phenomenon, although they just missed it in their curve 4, Fig. 2,

[1] Aschkinass and Schaefer, Ann. d. Phys., V., p. 489, 1901.

for a length 2 cm., twice the resonance length. Had they used an aperture in their diaphragm somewhat larger than 20 cm. on a side they doubtless would have found it. For the other curves the number of resonators used of double the resonance length was entirely too small and the side-on distance between them too great to show the effect. Nor does the fact that they didn't find it presuppose, as Schaefer argues, "large errors of observation" on their part.

Dr. Schaefer's second objection to our work lay in this, that when we changed resonator gratings, holding vibrator and receiver constant, we didn't change all distances and dimensions proportionately. He maintains, following the analogies[1] of optics, that in work with a resonator grating one can obtain correct results only when all dimensions of the grating are changed by the same relative amounts, using a constant vibrator and receiver. Before I can answer this objection I shall have to discuss the results that Schaefer obtained in his work[2] with resonator systems. With a constant resonator grating by means of a variable vibrator and receiver Schaefer determined the maximum absorption of a single column grating. By repeating this with a grating differing from the first only in that the resonators were closer together, he observed that the absorption maximum was displaced toward the smaller wave-lengths. By considering two adjacent resonators Schaefer explains this result theoretically as follows. Since the two resonators are entirely identical, if we represent the resistance, self-induction, mutual induction and capacity of each of the resonators by w, L_{11}, L_{12}, C respectively, these differential equations hold:

$$\frac{d^2i_1}{dt^2} + \frac{w}{L_{11}}\frac{di_1}{dt} + \frac{i_1}{L_{11}C} = -\frac{L_{12}}{L_{11}}\frac{d^2i_2}{dt^2},$$

$$\frac{d^2i_2}{dt^2} + \frac{w}{L_{11}}\frac{di_2}{dt} + \frac{i_2}{L_{11}C} = -\frac{L_{12}}{L_{11}}\frac{d^2i_1}{dt^2},$$

where i_1 and i_2 are the currents in the two resonators at the time t. Neglecting the resistance term the general integral is of the form

[1] For a view upon the closeness of these analogies see Webb and Woodman, PHYS. REV., Vol. XXIX., p. 90, 1909.

[2] Clemens Schaefer, loc. cit.

$$i_1 = A \cos 2\pi \left(\frac{t}{T_1} + \delta_1\right) + B \cos 2\pi \left(\frac{t}{T_2} + \delta_2\right),$$

$$i_2 = A \cos 2\pi \left(\frac{t}{T_1} + \delta_1\right) - B \cos 2\pi \left(\frac{t}{T_2} + \delta_2\right),$$

where A, B, δ_1, δ_2 are constants of integration and

$$T_1 = 2\pi \sqrt{(L_{11} + L_{12})C}, \quad T_2 = 2\pi \sqrt{(L_{11} - L_{12})C}.$$

Schaefer then says that since the two resonators are wholly identical and since, for both, the initial conditions are the same it follows that $i_1 = i_2$, that is, that $B = 0$ and hence that

$$i_1 = i_2 = A \cos 2\pi \left(\frac{t}{T_1} + \delta_1\right).$$

Thus the free period of vibration of a resonator

$$T_0 = 2\pi \sqrt{L_{11} C_0},$$

is altered by the presence of the second resonator to the period T_1 above. Schaefer says further, "In distinguishing between T_1 and T_2 it must not be overlooked that the capacity C_0 is changed by the approach of the second resonator." By writing $i_1 = i_2$ he thus arbitrarily drops T_2, the second possible[1] period of vibration, and so *is forced* to explain the displacement of the absorption maximum upon the approach of the second resonator by the lowering of the capacity, that is, "as if $L_{12} = 0$." No wonder Schaefer found that in each of the twenty gratings that he worked with the influence of the capacity factor far exceeded that of the mutual induction! Surely, in considering the effect upon the absorption maximum of the approach of a second resonator, one cannot rightly do else than say that i_2 in the differential equations above is the current in the second resonator due to the impressed electromotive force in the first resonator. It is true, of course, that the total current in each resonator is the same, for their mutual effects are the same and both are subject to the same external force of the wave. But

[1] See A. Oberbeck, Ann. d. Phys., Vol. 55, p. 624, 1895, or Fleming, "Principles of Electric Wave Telegraphy," 1st edition, p. 209.

it is the mutual effects *alone* (in general *both* of capacity and induction) that enter into the question of the displacing of the absorption maximum.

Now it is well known[1] that the effective inductance of a circuit is *decreased* by the presence of a second circuit, and for currents of high frequency the amount of the effective inductance is $L_{11}-L_{12}^2/L_{11}$. That is, instead of Dr. Schaefer's value for T_1 above, the correct value should be

$$T_1 = 2\pi\sqrt{\left(L_{11}-\frac{L_{12}^2}{L_{11}}\right)C},$$

which shows that for two resonators approaching each other side-on, *both* the inductance and capacity tend to decrease the period. Now the fact that Curve *A*, Fig. 11, for Blake and Fountain was a straight line showed that the capacity of a resonator was practically unchanged by the *end-on* approach of a second resonator up to 5 mm. from the first. Accordingly we argued that for *side-on* approach of two resonators, since in our experiments they were never closer than 1 cm., any change in period must be attributed to inductance and not to capacity changes. By false theoretical considerations Schaefer was forced to explain the facts of experiment (which I do not at all deny) by capacity changes alone. I agree with him that for end-on approach one may safely take $L_{12} = 0$ and hence any change of period must be due to increase of capacity. If this is so I see no better way of trying to determine to what extent change of period is due to inductance and to what extent to capacity for side-on approach of resonators than by first determining within what limits changes of distance in end-on approach do not affect the capacity. This is what we did in curve *A*, Fig. 11, although I am free to say that we did not try this out in any thorough manner.

Only one other point in Schaefer's criticism needs to be mentioned. Is it necessary, as he insists, for satisfactory conclusions to be drawn, that in changing from one grating to another all dimensions and distances be changed relatively the same amount?

[1] See Maxwell, Phil. Trans., 1865. See also Lord Rayleigh, Phil. Mag., Vol. 21, p. 375, 1886.

I do not believe it is. Certainly one cannot stick too close to optical analogies in determining what are proper methods of experimentation. For, so long as optical resonators are in general very small compared with the wave-lengths they emit, while electrical resonators are comparable in size to the wave emitted, the analogies are certain to break down in many vital points just as Schaefer himself found to be the case in comparing the theory developed by Planck[1] with experiment.

In this connection Schaefer invites comparison between the curves of Blake and Fountain with those of Aschkinass and Schaefer as well as with his own. He insists that by keeping the same relative distances for all the gratings he and Aschkinass obtained relatively simple relations where we obtained complicated ones. Remembering that Blake and Fountain did not change the dielectric, what could be more simple than to expect minimum absorption for twice the resonance length? And yet for only two of the four curves does Fig. 2 of the work of Aschkinass and Schaefer show this minimum correctly. One has only to compare the character of their curve 2 with that of curve 3 for resonator lengths greater than 4 cm. to see how simple (?) the relation between them is. I venture the assertion that if Aschkinass and Schaefer had for all their gratings kept their resonators constant at 2 mm. width and the side-on distance between the resonators constant at 6 or 8 cm., then, starting with an end-on distance great enough so that capacity changes would not enter (say 2 cm.), had they proceeded to change the length only of their resonators they would have obtained the same ratio L_1 that their Table II. shows and far more satisfactory and comparable curves than their Fig. 2 shows.

Late as is the date, I believe that I have now satisfactorily refuted Schaefer's objections. It seems certain that the work of Blake and Fountain must stand practically as they left it. It remains only to say a word about Cartmel's paper.[2] Cartmel has endeavored to explain extra transmission on the ground that the phase relation between the energy reflected from the front and

[1] Planck, Sitzungsber. d. k. Akad. d. Wissensch. zu Berlin, Vol. I., p. 470, 1902; loc. cit., p. 480, 1903.

[2] Cartmel, PHYS. REV., Vol. XXV., p. 64, 1907.

back faces of the glass is affected by the presence of the resonators. I am unable at the present time to throw any light on the question as to which is the better explanation, Cartmel's or ours. Certainly it couldn't account for the *lens-action* of the resonator system. At most it could account for what I (as well as Cartmel) have called *true extra transmission*. But it seems no simpler than ours.[1]

I cannot close this paper without seconding the appeal made by Webb and Woodman[2] for a more systematic study of apparatus and conditions in the field of short electric waves. Certainly there have been great confusion and contradiction of experimental data and results. May we hope that in the future experimenters in this field will not take so much for granted as they have in the past.

To several of the teaching staff of the department I owe my best thanks for their help in various ways. Especially do I wish to thank Professor Kester, now of the University of Kansas, for much aid in taking the observations and for many valuable suggestions and criticisms.

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[1] Possibly Woodman and Webb (see PHYSICAL REVIEW, Vol. XXX., page 561, 1910) are right in saying that phase change and change in velocity necessarily accompany each other, and hence that the two explanations are the same. Perhaps further work will give us clearer notions on the *modus operandi* of what we term "change of phase."

[2] Webb and Woodman, loc. cit.

MAGNETOSTRICTION IN IRON-CARBON ALLOYS.

BY HERBERT G. DORSEY.

SINCE Joule's discovery in 1842 that iron changes its dimensions when magnetized, much experimental work has been done on this interesting phenomenon. But of the numerous articles published I have found none which gives a complete chemical analysis of an iron specimen.

The excellent series of steel rods of known analysis used by Dr. C. W. Waggoner[1] being available it seemed desirable to make tests on their changes in length in a magnetic field.

After studying the various magnifying devices used by different workers and as a result of a few preliminary trials the method used by Guthe and Austin[2] in their work on magnetostriction in Heusler alloys was employed with but few changes.

Fig. 1 gives a general view of the entire apparatus with details of the magnifier. The steel rod shown in black was soldered into the ends of brass rods B and B' and the latter was clamped rigidly at one end of the frame of brass tubing. At the other end of this frame was attached the wooden base of the magnifier. This consisted of a glass plate freely movable on roller bearings of needles. Two glass plates were fixed at right angles in a block of wood and the third larger plate was held to the vertical needles by a rubber band R. The two proximate vertical surfaces were ground together with fine emery and this seemed essential to prevent slipping in the greater changes of length. The rubber band not only holds the plate in place but presses it lightly against the rod B so that any motion of B is communicated to the glass plate. To one of the vertical needles was fastened a glass pointer P, which was made by drawing a glass tube very small, bending at right angles near the larger end and fastening the point of the needle into the tube with

[1] PHYS. REV., Vol. 28, p. 393, 1909.
[2] Bul. Bur. Stds., Vol. 2, p. 297, 1906.

sealing wax. Opposite this needle in a hole in the wooden block was placed a glass tube bent at right angles, the other end being drawn down to a point. This glass arm being thus pivoted near the rotating needle gives a method of quick rough adjustment without changing much the sensibility. To the ends of the glass arm and pointer were fastened two silk fibers which supported the

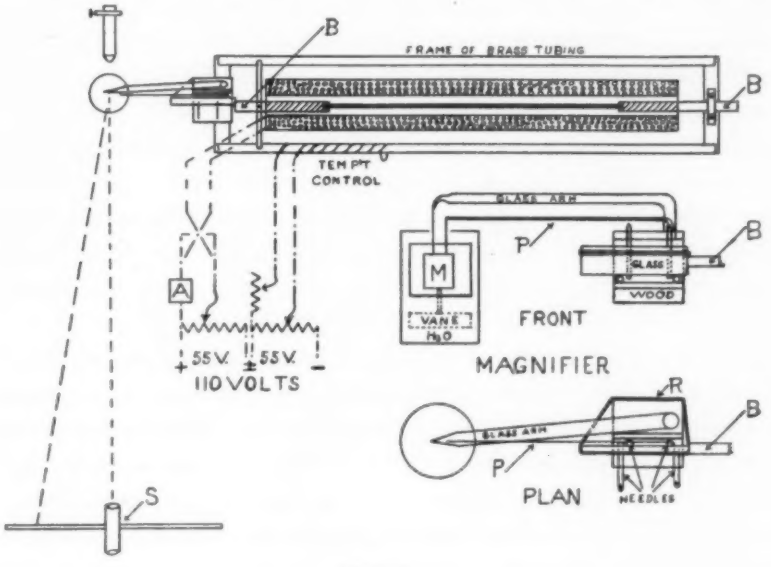

Fig. 1.

tiny mirror M. The mirror carried a small glass vane under water which rendered it nearly although not quite aperiodic. Mirror, vane and water were in a brass tube with glass window. The deflections of the mirror were observed by the telescope and scale.

If a = diameter of the needle = 0.0652 cm.
b = distance between threads = from 0.08 to 0.2 cm.
c = scale deflection.
d = distance scale to mirror, usually about 120 cm.
e = length of glass pointer = 6.90 cm.
l = length of rod tested,

then

$$\frac{\Delta l}{l} = \frac{abc}{2del}.$$

Scale deflections could be easily read to 0.1 cm. so that the smallest change in length which could be easily detected was

$$\frac{abc}{2de} = \frac{.0652 \times .08 \times .01}{2 \times 120 \times 6.90} = 3.15 \times 10^{-7} \text{ cm.}$$

At first a number twelve needle of 0.035 cm. diameter was used and a pointer 15 cm. long, but the magnifier was so much more sensitive than was necessary for such long rods that the larger needle and shorter pointer were chosen. With all of its high magnification, the parts were all so light that there seemed to be no lost motion of any sort and there was no appreciable trouble from vibrations. The entire apparatus was tested with a brass rod in the place of the iron rod and absolutely no effect was observable when the strongest magnetizing current was applied.

TEMPERATURE COMPENSATION.

With a magnification of 300,000 a change in temperature of one degree for a 40 cm. rod would produce a deflection of more than a hundred scale divisions so that efforts to maintain a constant temperature were soon abandoned and compensation was employed. On the side tubes of the brass frame a few turns of fine insulated advance wire were wound, through which was sent a small current which could be closely adjusted by means of the shunt and rheostat shown in Fig. 1. This current warmed the brass frame and by its expansion the magnifier was moved forward an amount equal to the increase in length of the steel rod due to temperature changes. The changes in length due to magnetism are so nearly instantaneous and the magnifier responds so quickly that no trouble was experienced in getting readings before temperature produced any effect. In any case the temperature changes produce slow drifts while the magnetism changes are sudden, so that there is no difficulty in distinguishing between the two. With the harder steels the warming due to hysteresis of a single reversal of a current of one ampere could be detected.

MAGNETIZATION.

The magnetizing coil contained 2,240 turns of number 10 copper wire wound on a brass tube of 1.1 cm. external diameter and 70

cm. length. An alternate current of about 50 amperes was sent through it a few minutes while containing an iron core as a test for short circuits, for if there were any the short-circuited turns would get hotter than the rest of the coil. The heating was uniform, indicating no short circuits, but the coil length contracted permanently to 69.5 cm. The calculated value of the field strength is 40.5 gausses per ampere. This was checked by a small exploring coil, the same one described later, in two other long slim solenoids and the calculated values for all three differed by less than one per cent. The coil was then explored with the test coil and for a distance of over 40 cm. the field varied by not more than 1.3 per cent.

Current was taken from a motor generator set having nearly perfect automatic regulation of field excitation. To one side of the 55-55-110-volt circuit was shunted a tin resistance frame and from this 28 wires were connected to a dial switch so that currents through the magnetizing coil could be varied by steps from 0.05 to 42.5 amperes. Currents were measured by a Weston milli-voltmeter with two shunts, one for currents 0 to 5 amperes, the other 0 to 50 amperes.

All values of field strength H and magnetic intensity I, unless otherwise noted, are corrected for the demagnetizing effect of the ends of the rods. These corrections for H vary from 15 per cent. for $A3$ to more than 100 per cent. for PI. The values of m = length/diameter are given in Table X. Magnetization curves were taken by the ballistic method. The ballistic coil already mentioned as a test coil consisted of 185 turns of number 40 wire wound upon a brass tube of 0.80 cm. external diameter. The coil length was 3.1 cm. The galvanometer was of the D'Arsonval type of medium period and large damping. It was calibrated by means of the test coil used in two different long solenoids with several different currents measured by the same ammeter used in the rest of the work. A line was plotted from these different values and the galvanometer constant determined from the slope of the curve. It was also checked by a standard cell and condenser, proper corrections for logarithmic decrement being made for all measurements.

In taking data for the magnetization curves the specimen was

first demagnetized by reversals and then the desired current reversed at least 25 times before the galvanometer throw was recorded and a second reading taken as a check. The current was then increased, 25 more reversals made and the throw recorded and this process repeated until the entire range was covered. With the harder steels 35 to 40 reversals were necessary. This approximately gives what C. W. Burrows[1] calls a normal magnetization curve.

In order to find the correction to be applied to the values of H for the length of ballistic coil used a magnetization curve for PI was made by the magnetometer method, and corrections applied for the demagnetizing effects of the rod ends according to the method of C. R. Mann.[2] The corrected curve was then plotted along with the curve made by the ballistic method and their differences found, from the average of which it appeared that if Mann's values of the correction factor N were divided by 1.66 the corrected values of I could be found up to $I = 800$. Above this value a sliding scale was used, and it is believed that the corrected values are not far from the truth. The values of N for the different specimens are given in Table X. This method of making corrections appears to be reliable for it is checked by an entirely different method. In Fig. 7, where the uncorrected susceptibility of $D1$ and $D2$ are plotted as a function of diameter divided by length these curves cross the Y axis at $K = 141$ and 115 respectively, which would represent the values in rings or rods without poles, and the values by correction are 139 and 113 respectively. The magnetic tests were made after the magnetostriction tests. To find values of I and H corresponding to values of current used in the magnetostriction tests large curves were plotted for each specimen and values taken from them.

The value of I, the intensity of magenetism, is given by the formula

$$I = \frac{\frac{\varphi}{n} - AH'}{4\pi\alpha - AN},$$

[1] Bul. Bur. Stds., Vol. 4, p. 205, 1908.
[2] PHYS. REV., Vol. 3, p. 367, 1895.

in which 2φ is the change in flux for a reversal of the current, n is the number of turns of the ballistic coil, = 185, A is the area of the ballistic coil, = 0.503 sq. cm., α = area of the specimen, N = the correction factor, and H' = uncorrected field strength = 40.5 × current in amperes.

$$2\varphi = q_0\delta(1 + \lambda/2)R \times 10^8,$$

in which q_0 = the quantity constant of the galvanometer = 100.7 × 10^{-9}, δ = the throw of the galvanometer, λ = the logarithmic decrement and R = the total resistance in the circuit. For any given specimen the above formula reduces to

$$I = a\delta(1 + \lambda/2)R - b \times \text{current},$$

where a and b are constants.

Specimens.

The rods were first tested in the following condition as received from Dr. Waggoner. They were about 40 cm. long and about .5 cm. in diameter, the ends being drilled longitudinally for about .5 cm. for lathe centers when they were turned down from the original rods. They were then annealed at 1000° for two hours and his magnetic tests made at room and liquid air temperatures. The chemical analysis is here repeated as given in his paper.

Chemical Analysis.

Mark.	C	P	Si	Mn	S
P.I.	.058	Trace	.008	.071	—
A1	.60	.013	.15	.14	.012
A2	.74	.012	.16	.14	013
A3	.89	.010	.19	.155	.013
A4	.98	.012	.16	.15	.013
A5	1.18	.012	.14	.14	.013
A55	1.26	.012	.16	.17	.014
A6	1.37	.011	.19	.16	.012

Magnetostriction Tests.

The following procedure was taken in all measurements on magnetostriction. The specimen being placed in the coil and adjustments made was demagnetized by reversals. The desired current applied

and deflection and current noted. Specimen again demagnetized and the same current applied in the opposite direction and deflection noted. This was then repeated, thus giving four readings for each step of the current. The deflections given in the following tables are the average of four measurements, each taken with the current in a direction opposite to that used in the preceding measurement. The last three scale deflections are exceptions and are the average of only two measurements on account of excessive heating of the higher currents.

TABLE I.

PI, 0.058 *Per Cent. Carbon.* $b=0.2892$ *cm.*, $d=120.5$ *cm.*, $l=39.5$ *cm.*

H	I	$\Delta I/I$	H	I	$\Delta I/I$
1.96	270	$.17\times10^{-6}$	63.9	1,308	3.24×10^{-6}
2.93	486	.37	73.0	1,322	3.10
4.33	712	.83	93.7	1,350	2.76
5.00	800	1.26	142.5	1,414	1.81
6.49	924	1.64	214.	1,486	.32
7.80	1,022	2.04	242.	1,511	− .26
11.00	1,115	2.50	300.	1,545	−1.55
14.0	1,163	2.84	352.	1,572	−2.57
18.4	1,202	3.13	493.	1,611	−4.88
24.0	1,230	3.30	580.	1,624	−5.57
29.2	1,244	3.39	757.	1,643	−6.58
36.8	1,260	3.45	1,090.	1,660	−7.41
44.3	1,278	3.45	1,580.	1,675	−8.05
52.0	1,292	3.39			

TABLE II.

*A*1, 0.60 *Per Cent. Carbon.* $b=0.1568$ *cm.*, $d=120.5$ *cm.*, $l=39.5$ *cm.*

H	I	$\Delta I/I$	H	I	$\Delta I/I$
4.7	263	$.14\times10^{-6}$	77.6	1,184	1.78×10^{-6}
6.8	413	.28	110.	1,240	1.41
8.1	490	.43	157.	1,298	.74
9.6	572	.56	194.	1,334	.16
11.4	653	.71	214.	1,344	− .11
14.0	760	.89	239.	1,370	− .50
17.7	870	1.07	272.	1,395	−1.03
24.0	972	1.45	353.	1,434	−2.30
30.0	1,022	1.54	428.	1,472	−3.17
36.4	1,058	1.67	583.	1,520	−4.76
43.0	1,090	1.68	770.	1,550	−5.80
49.6	1,120	1.70	1,190.	1,595	−6.63
59.5	1,150	1.73	1,685.	1,640	−7.35

TABLE III.

A2, 0.74 Per Cent. Carbon. b=0.1205 cm., d=121 cm., l=39.6 cm.

H	*I*	$\Delta l/l$	*H*	*I*	$\Delta l/l$
5.0	180	$.02\times10^{-6}$	61.5	1,162	1.40×10^{-6}
6.4	280	.07	70.1	1,180	1.39
8.0	386	.15	90.1	1,215	1.28
9.0	450	.20	138.	1,280	.76
10.5	526	.27	205.	1,346	− .12
13.4	650	.40	230.	1,365	− .44
15.7	732	.56	290.	1,404	−1.24
20.5	840	.77	342.	1,430	−1.90
25.8	922	.95	490.	1,482	−3.40
30.1	974	1.06	575.	1,503	−3.94
37.5	1,044	1.19	760.	1,532	−4.85
43.5	1,076	1.31	1,110.	1,571	−5.55
50.9	1,127	1.38	1,660.	1,618	−6.11

TABLE IV.

A3, 0.89 Per Cent. Carbon. b=0.1385 cm., d=120 cm., l=39.4 cm.

H	*I*	l/l	*H*	*I*	$\Delta l/l$
9.0	228	$.01\times10^{-6}$	73.5	1,130	$.68\times10^{-6}$
10.5	290	.03	90.0	1,175	.62
12.5	375	.04	138.	1,268	.29
16.6	545	.07	207.	1,333	.37
17.3	552	.14	230.	1,350	− .68
22.5	700	.24	290.	1,385	−1.37
28.0	790	.32	347.	1,410	−1.86
32.5	850	.40	482.	1,456	−3.07
39.5	928	.49	568.	1,474	−3.64
46.5	988	.56	760.	1,510	−4.52
54.0	1,036	.62	1,100.	1,550	−5.45
65.0	1,095	.67	1,635.	1,615	−6.11

In Fig. 2 the percentage change in length is plotted as a function of *H* for the first five rods of the series. The others are not plotted as they are so close to *A2* that plotting them in this figure would only tend to produce confusion.

Fig. 3 shows the relation between magnetostriction and the intensity of magnetization.

Data for residual magnetostriction curves are plotted for specimens *A4* and *A6* in Fig. 4. To get these a reading of the telescope

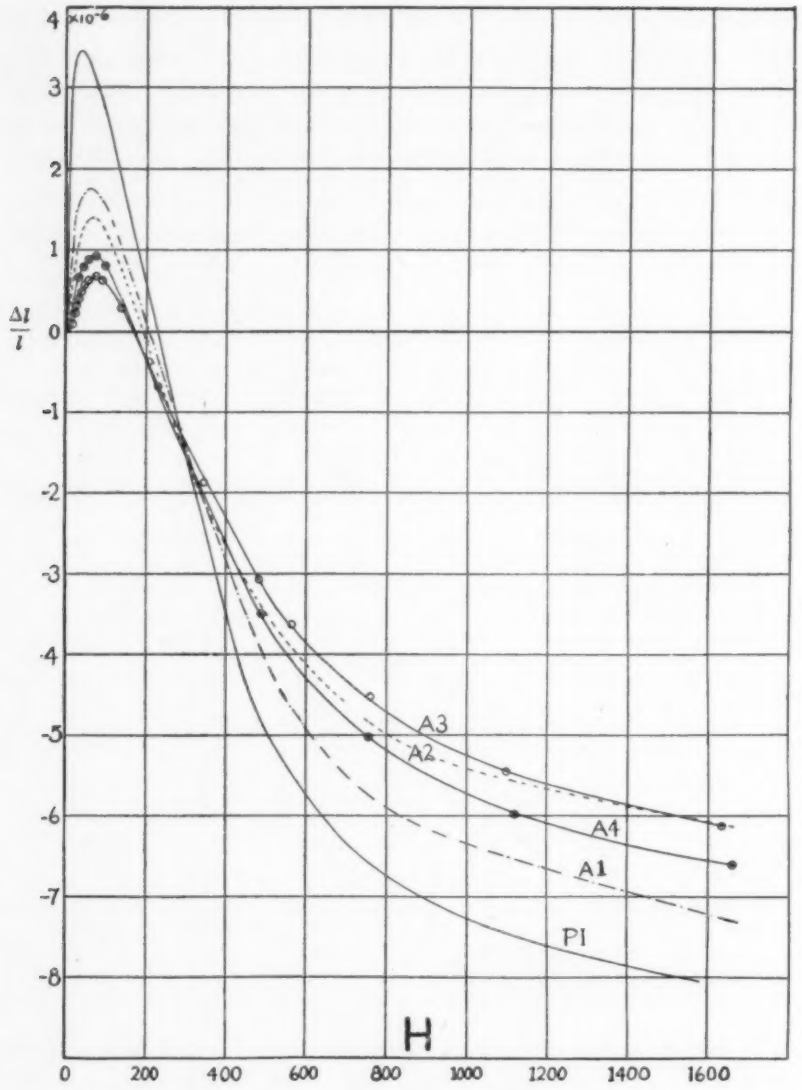

Fig. 2.

Magnetostriction as a function of field strength.

was made after the circuit was broken and as the deflection is then in the opposite direction as when the circuit is closed deflections for residual are recorded with an opposite sign. In the specimens magnetically soft scarcely any residual effect could be found but

those which are harder remain longer after being magnetized unless the actual field strength reaches about 400 or more.

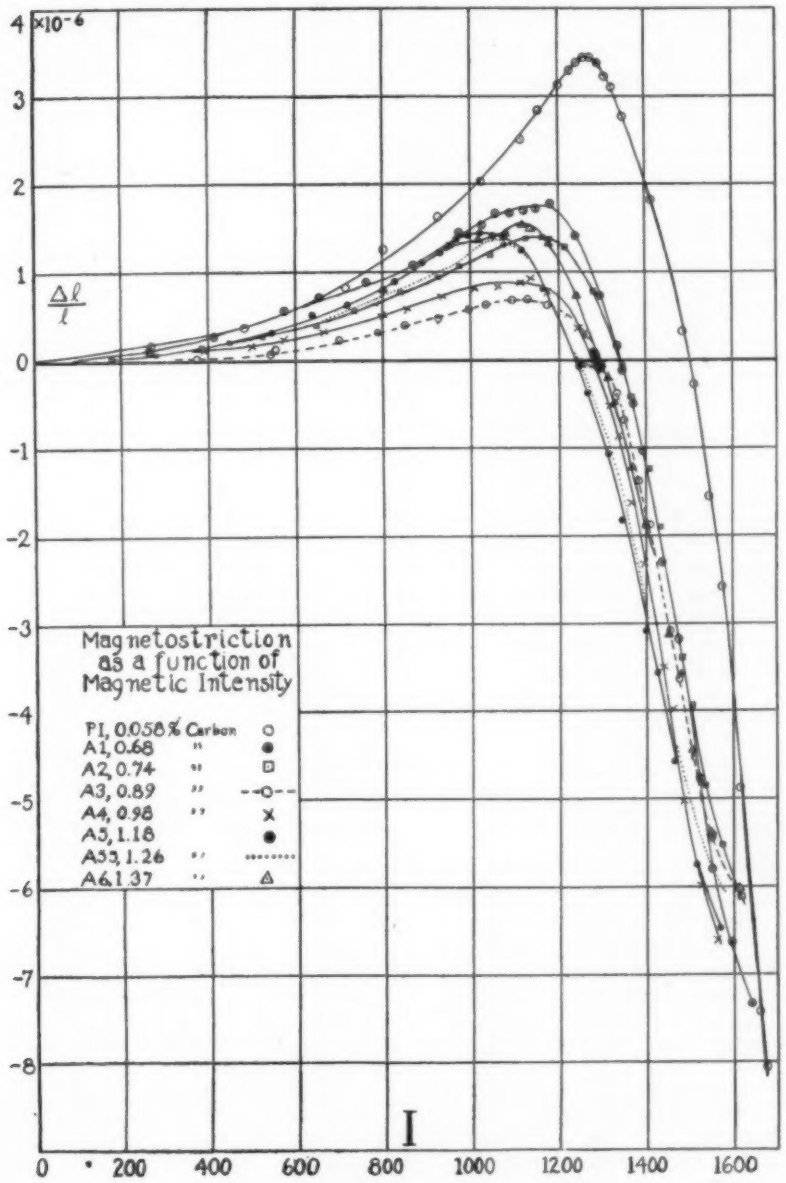

Fig. 3.

TABLE V.

A4, 0.98 Per Cent. Carbon. $b=0.1568$ cm., $d=120.5$ cm., $l=39.5$ cm.

H	I	$\Delta l/l$	Residual.	
			Deflec.	$\Delta l/l$
8.6	244	$.02\times10^{-6}$		
9.8	300	.05		
11.7	390	.11		
14.4	500	.17	− .5	$.09\times10^{-6}$
16.4	575	.25	− .7	.14
19.5	665	.34	− .8	.22
26.2	800	.51	− 1.7	.25
30.0	854	.59	− 1.9	.30
36.3	932	.73	− 2.5	.34
44.5	1,008	.81	− 3.0	.34
52.3	1,060	.84	− 3.5	.30
63.4	1,110	.89	− 3.3	.34
71.7	1,137	.92	− 3.6	.34
92.0	1,173	.76	− 3.0	.30
138.	1,245	.36	− .8	.23
211.	1,315	− .53	+ 5.1	.26
235.	1,335	− .86	+ 6.8	.20
290.	1,367	−1.62	+11.8	.19
350.	1,395	−2.33	+16.0	.15
490.	1,440	−3.50	+23.4	.14
578.	1,460	−3.98		
758.	1,488	−5.01		
1,120.	1,528	−6.98		
1,660.	1,562	−6.60		

TABLE VI.

A5, 1.18 Per Cent. Carbon. $b=0.1036$ cm., $d=120.5$ cm., $l=39.6$ cm.

H	I	$\Delta l/l$	H	I	$\Delta l/l$
7.30	270	$.06\times10^{-6}$	74.5	1,073	1.40×10^{-6}
8.50	345	.13	98.	1,116	1.25
9.51	422	.20	143.	1,167	.77
11.5	542	.32	215.	1,248	− .07
13.5	638	.51	238.	1,267	− .37
16.0	718	.64	300.	1,314	−1.06
21.0	824	.90	352.	1,344	−1.82
26.2	890	1.11	495.	1,400	−3.08
31.6	930	1.23	580.	1,425	−3.56
38.0	964	1.36	780.	1,463	−4.56
45.8	996	1.43	1,147.	1,513	−5.75
53.7	1,020	1.45	1,680.	1,570	−6.48
65.6	1,050	1.43			

TABLE VII.

A55, 1.26 Per Cent. Carbon. $b=0.1568$ cm., $d=120$ cm., $l=39.5$ cm.

H	I	$\Delta l/l$	H	I	$\Delta l/l$
7.73	195	$.03\times10^{-6}$	78.0	1,107	1.26×10^{-6}
8.75	275	.06	100.	1,140	1.15
10.0	370	.11	148.	1,193	.59
11.8	465	.20	212.	1,265	− .23
14.7	595	.36	238.	1,285	− .50
17.0	678	.48	295.	1,322	−1.14
22.0	790	.72	353.	1,352	−1.73
27.2	867	.87	490.	1,400	−3.02
32.6	928	1.00	580.	1,425	−3.43
39.3	980	1.12	775.	1,460	−4.27
46.0	1,018	1.17	1,120.	1,508	−5.14
53.8	1,050	1.37	1,660.	1,575	−6.01
63.7	1,080	1.30			

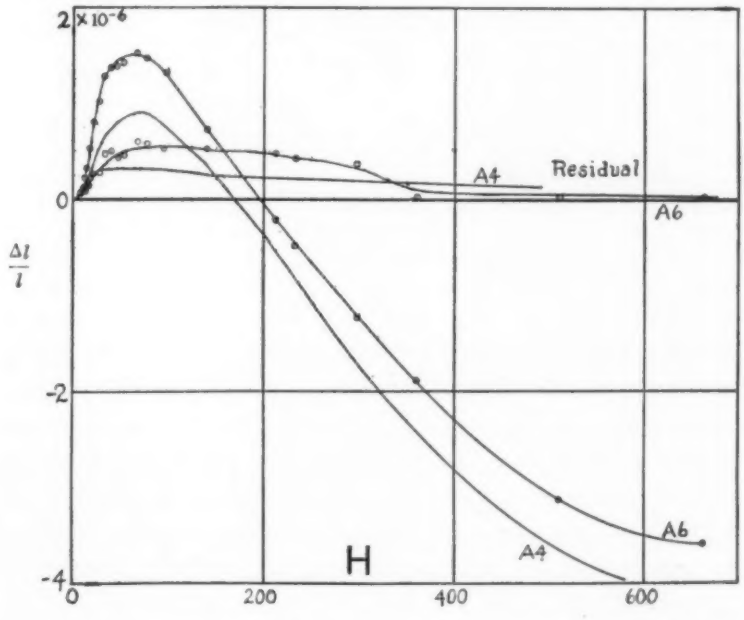

Fig. 4.

IN WHAT PORTION OF A ROD IS THE CHANGE IN LENGTH GREATEST?

Since iron gets longer for weak intensities of magnetization and shorter for stronger intensities in might be asked if all parts of a

TABLE VIII.

A6, 1.37 Per Cent. Carbon. b=0.1399 cm., d=119.5 cm., l=39.4 cm.

H	I	$\Delta l/l$	Residual.	
			Deflec.	$\Delta l/l$
8.8	270	$.06\times10^{-6}$	− .2	$.03\times10^{-6}$
10.4	368	.11	− .6	.03
12.3	476	.21	− .9	.08
15.0	600	.37	− 1.5	.15
16.9	674	.53	− 2.3	.21
21.5	800	.80	− 3.5	.31
27.0	898	1.01	− 4.9	.32
32.5	950	1.28	− 5.8	.46
40.0	1,012	1.37	− 6.2	.50
46.5	1,050	1.39	− 6.8	.44
54.1	1,080	1.42	− 6.9	.45
66.0	1,115	1.54	− 6.7	.60
75.6	1,136	1.49	− 6.4	.59
96.5	1,180	1.32	− 5.7	.52
140.	1,240	.72	− 1.4	.52
212.	1,313	− .20	+ 4.9	.49
233.	1,330	− .48	+ 6.4	.42
298.	1,368	−1.21	+11.2	.36
360.	1,400	−1.88	+13.5	.01
510.	1,450	−3.12	+22.0	.03
662.	1,480	−3.59	+25.7	.01
780.	1,502	−4.45		
1,114.	1,545	−5.40		
1,700.	1,610	−6.04		

rod are changing by the same amount when magnetized. To investigate this question several determinations were made by soldering slotted tubes on *PI* at equal distances from the center so as to leave the rod its original length and yet test the change in length for different portions of the rod. Only enough points were determined to find the maximum elongation although the maximum current was turned on each time to see that the retractions of the rod were about the same no difference what portion was tested.

After these tests were made a ballistic coil of a single layer was wrapped over one half of the rod and leads taken off at different portions so as to have the equivalent of several test coils of different lengths on the rod. It was assumed that the magnetism would be symmetrically distributed on each side of the rod center. A nor-

mal magnetization curve was then taken, the galvanometer being switched to the different test coils for each point. The maximum susceptibilities without any correction for end effects were thus determined for each of the different coils. These values are given in Table IX. and plotted in Fig. 5. It will be seen that the elonga-

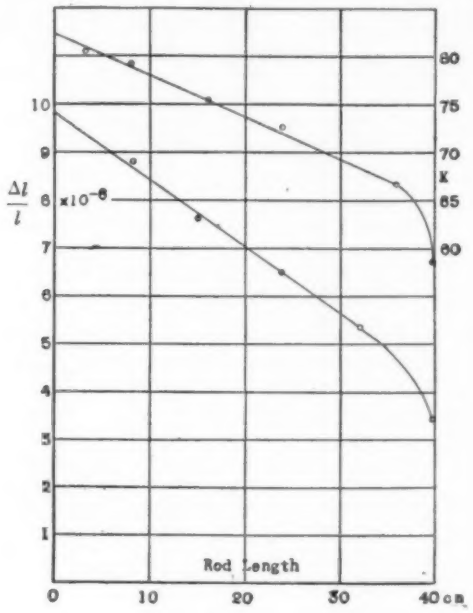

Fig. 5.

Maximum percentage elongation and maximum apparent susceptibility of PI as functions of the length of rod tested.

tion and apparent susceptibility increase regularly as the center of the rod is approached although there is a sudden decrease in both near the end of the rod. As would be expected, the different points of maximum elongation and points of maximum apparent susceptibility occurred at the same values of H as they did when the full rod length was tested, viz., $H = 44.3$ for magnetostriction and $H = 2.93$ for susceptibility.

Effect of Length of Rod.

In order to preserve the rods of the series another rod was taken for this test. It was of soft iron and cut to the same size as the

others and annealed. It was called *D*1. After tests were made on the full length portions were cut from the end after each test so that eight different lengths were used. Values are given in Table IX. and in Fig. 6 maximum apparent susceptibilities and maximum

TABLE IX.

P1, Full Length, First Condition. $\Delta l/l$ and Uncorrected Susceptibility Tested in Different Portions of the Rod.

Length.	$\Delta I/I$ Max.	Coil Length.	k Max. (n.c.).
39.8 cm.	3.45×10^{-6}	39.8 cm.	58.6
32.0	5.35	35.9	66.6
23.9	6.50	23.8	72.6
15.0	7.62	16.0	75.5
8.1	8.80	8.0	79.2
7.9	9.15	3.1	80.5

D1, Soft Iron, No Analysis. Annealed and then Cut to Various Lengths. Diameter = 0.58 *cm. Corrected* $k = 139.5$.

Length.	Diameter / Length	$\Delta I/I$ Max.	k Max. (n.c.).
39.8 cm.	.0146	4.78×10^{-6}	75.1
35.0	.0166	4.08	65.5
30.0	.0193	3.93	54.3
25.0	.0232	2.23	42.8
22.0	.0263	1.87	38.6
20.0	.0290	3.19	30.8
12.0	.0474	2.33	
4.8	.121	1.90	
∞	0 from curve	5.80	141.

D2, Soft Steel, No Analysis. Eight Pieces Cut from the Same Rod. Ends Threaded and then Annealed in Nitrogen. Diameter = 0.638 *cm. Corrected* $k = 113$.

Length.	Diameter / Length	$\Delta I/I$ Max.	k Max. (n.c.).
40	.0160	3.10	62.9
35	.0182	3.32	54.7
30	.0213	2.90	43.9
25	.0255	2.85	34.4
20	.0319	2.78	24.4
15	.0425	2.70	16.1
10	.0638	2.40	8.7
5	.128	2.35	3.15
∞	0 from curve	3.80	115.

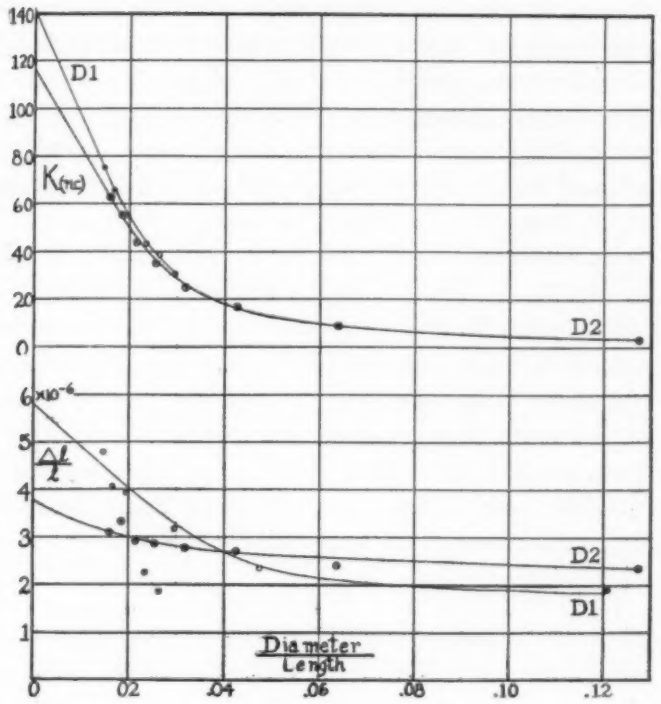

Fig. 6.

percentage elongations are plotted as functions of diameter divided by length. It will be noticed that two points for magnetostriction are far from the curve, but these are thought to be due to accidenta-conditions of the iron rather than to errors of measurements. All though carefully taken at the time they could not be checked afterwards as the rod had been made shorter. The rods were each time soldered to the brass end rods and the temperature reached in soldering might have been sufficient to have altered the condition. To avoid this another series of rods was made from a single long rod of commerical soft steel called *D2*. The ends were threaded so as to avoid soldering and then all were heated to 1000°C. in an atmosphere of nitrogen and furnace cooled. Each rod was then tested as before.

It should be noted that for the shorter rod lengths it required a much higher apparent field strength, uncorrected for end effects,

to produce the maximum elongations. Thus for $D1$ full length maximum elongation occurred at apparent $H = 60$ while for the 4.8 cm. length it required apparent $H = 145$. For $D2$ the corresponding values are 54 and 243. These results quite confirm those of Sidney Lochner,[1] who showed that a short thick rod apparently expands for all fields only because the actual field strength is small due to the demagnetizing effects of the ends.

The values obtained for $D1$ and $D2$ are given in Table IX. and curves in Fig. 6. If these curves are projected back to cut the Y axis we have values for rods of infinite length as compared to their diameters, comparable to a ring without poles. As before mentioned the values of susceptibility check almost exactly with those obtained by making corrections for end effects. From similar reasoning then, a steel of the quality of $D1$ in the shape of a ring would have a maximum percentage elongation along the circumference of 5.8×10^{-6} and for steel of the quality of $D2$ it would be 3.8×10^{-6}.

MODULUS OF ELASTICITY.

Having found a close relationship between maximum elongation and maximum susceptibility it was thought desirable to see if there is any relation to the modulus of elasticity. This was tested by means of an Olsen testing machine and a mirror extensometer reading to 1/40,000 inch. The values are given in dynes per square cm. in Table X. and plotted as a function of the carbon content in Fig. 7. These values are in good general agreement with those found by Benedicks.[2]

It will be noticed that there is a general tendency for the curve to slope downwards for the higher per cent. carbon. Also that the retraction curve for a value of $H = 1{,}500$ has a general slope upwards so that roughly we can say that the amount of shortening in a strong field varies directly as the modulus of elasticity, a result exactly opposite to what I expected to find.

EFFECT OF HEAT TREATMENT.

To remove any possible hardening effect due to stretching during the modulus tests the specimens were annealed at about 800° and

[1] Phil. Mag., Vol. 36, p. 504, 1897.

[2] Reserches Physiques et physico chemiques sur l'acier au carbone. Carl Benedicks, Upsala, 1904.

furnace cooled. Curves were again taken which had the same general shape as those already given but there was a notable change in the maximum values for $A55$ and $A6$ both for magnetostriction and susceptibility. Both values had increased. PI had also increased very materially for magnetostriction with apparently no change in susceptibility, although only a rough test was made of it

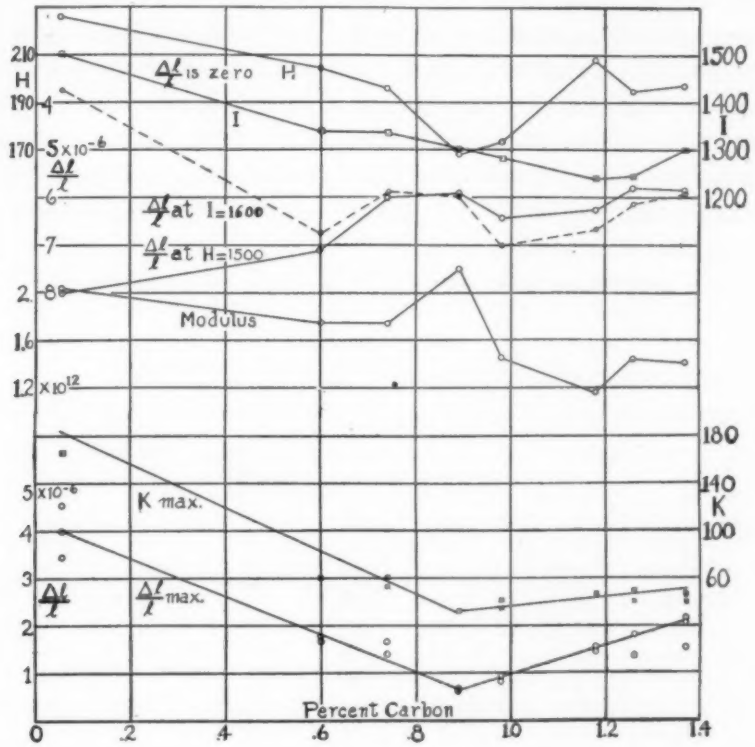

Fig. 7.

for this specimen. PI, $A3$ and $A6$ were then heated to about 1000° and quenched in water and tests made. PI and $A6$ were again annealed at 1000° and furnace cooled and $D1$ had been carried through the same process before being cut down. These values are all given in Table X. and plotted in Fig. 5 as a function of the per cent. carbon. The new values for $A55$ and $A6$ point to a probability that they were not entirely annealed in their first condition, and with the exception of PI and $D1$ it may be said that quenching or

sudden cooling lowers the amount of maximum elongation while annealing raises it. This is in accordance with Joule's third law, that "the elongation is for the same intensity of magnetism proportional to the softness of the metal, greatest in iron, least in hard steel." *PI* and *D*1 which were soft iron both confirm and deny this general truth. For each in one so-called annealed condition gave values higher than in the quenched state. But, on the other hand, each in a quenched condition gave values higher than in one so-called annealed condition. I think this simply points to the fact that annealing in soft iron at least is not definitely stated until the exact temperature is stated, how long it is held at that temperature and how long a time is required in cooling. Some physical chemists claim that 5,000 hours at 1000° is necessary to anneal iron-carbon alloys.

This anomalous case for soft iron has also been reported by

TABLE X.

Collected Data for the Different Specimens.

	m	N	$E\times10^{12}$	First Condition.		Annealed.		Quenched.		Annealed.	
				$\Delta l/l$ max.	k max.	$\Delta l/l$ max.	k max.	$\Delta l/l$ max.	k max.	$\Delta l/l$ max.	k max.
PI	66	.00663	2.02	3.45	166.	4.52		3.49	90.3	3.59	222.
*A*1	73	.00542	1.75	1.78	60.6	1.70					
*A*2	65	.00680	1.75	1.40	52.4	1.68	60.8				
*A*3	74	.00530	2.20	.68	32.8	.63		.26	10.9		
*A*4	64	.00693	1.45	.92	35.1	.81	42.3				
*A*5	66	.00663	1.16	1.45	47.3	1.54					
*A*55	70	.00595	1.44	1.37	40.5	1.80	49.8				
*A*6	68	.00608	1.41	1.54	40.0	2.08	46.4	1.21	20.9	2.15	46.9
*D*1	69	.00603				2.78	154.	3.55	91.8	4.78	139.5

Shelford Bidwell[1] who found one soft iron ring which in the "annealed" condition contracted for all values of field strength. He considered this a rare specimen, and was unwilling to quench it for fear he could not reproduce the unusual condition.

ACCURACY.

It is believed that errors in all measurements of length were not greater than 0.3 per cent. and there were five such measurements

[1] Proc. Roy. Soc., Vol. 56, p. 94, 1894.

entering into the computations. Single readings of deflections may have been in error by from 0.5 per cent. to 3 per cent., depending upon the amount of deflection, but as these were mostly the average of four readings the error might be considered 1.5 per cent. Combining by square root of sum of squares gives 1.6 per cent. for measurements of magnetostriction. In the magnetic work currents may have been in error by 1 per cent., magnetic deflections on the average by 0.4 per cent., areas of rods and test coil by 0.6 per cent. each, resistances by 0.2 per cent., magnetic constants by 0.3 per cent. and field strength variation 1.3 per cent., giving a possible total error of 1.8 per cent. which is about the same as the discrepancy between the two different methods of arriving at the maximum susceptibilities of $D1$ and $D2$.

Conclusions.

From these experiments upon this series of iron-carbon alloys the following conclusions may be drawn:

1. The maximum elongation decreases with the carbon content to 0.9 per cent. carbon and then increases and may be represented by the equation

$$(\Delta + 4C - 4.2)(\Delta - 3.1C + 2.13) = 0,$$

in which $\Delta = \Delta l/(l \times 10^8)$ and C = per cent. carbon. Likewise the maximum susceptibility may be represented by the equation

$$(K + 185C - 194)(K - 40C + 4) = 0,$$

in which K = maximum susceptibility and C = per cent. carbon.

2. In a somewhat similar manner but not so definitely does the value of H at which the rods retract to their original length drop to a minimum value at about 0.9 per cent. carbon.

3. $\Delta l/l$ is practically the same, at a value of -1.4×10^{-6} for about $H = 300$.

4. Up to field strengths of about 1,600 the rods were still contracting at individual uniform rates. But for a field strength of 1,500 it may be said in a general way that the greater the carbon content the less the retraction. Also, the modulus of elasticity decreases with carbon. Or, the amount of shortening in strong fields varies directly as the modulus.

5. Steels slowly cooled have greater elongations and susceptibilities than when quenched. Accidental exceptions for soft iron. Magnetostriction depends upon the previous history of the specimen.

6. The percentage elongation in the middle of a 40-cm. rod of soft iron is nearly three times as much as for the entire rod.

7. Rods of different lengths of the same quality iron give different values, therefore

8. Absolute values of magnetostriction as determined by different workers cannot be comparable with each other unless experiments are made with rings or else some method of correction is devised.

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THE POINT DISCHARGE IN AIR FOR PRESSURES GREATER THAN ATMOSPHERIC.

BY O. AMSDEN GAGE.

THE effect of changes in pressure upon the ionization of gases has been quite extensively studied at pressures less than an atmosphere, but not so much attention has been paid to the higher values. The first workers in this field studied the change in spark potential difference and a number of such papers[1] has been published. The results obtained are most contradictory except that the relation between potential difference and gas pressure is a linear one up to 8 or 10 atmospheres. Above that, nothing consistent has been found.

Recently there has appeared a series[2] of papers on the effect of increased pressure upon ionization due to radium; all showing that, up to at least 17 atmospheres, the leakage current increases; in some cases the relation is practically linear. W. Wilson[3] has studied the increase in natural ionization of a closed vessel and also finds this linear relation for pressures greater than 4 atmospheres.

In planning the present work, the intention was to examine the change in disruptive discharge with pressure, but it was found desirable to use instead the point discharge studying the relation between current and potential difference. This particular form of discharge has been carefully investigated by a number of observers, but only Tamm[4] and Ewers[5] have studied to any extent the effect of pressure, and that for values less than one atmosphere. Instead

[1] Wolf, Wied. Ann., 37, p. 306, 1889. De Hemptine, Bull. de Belg., p. 603, 1903. Cassinto and Occhiatini, Rend. R. Acc. dei Linc., 15, p. 715, 1906. J. J. Thomson, Cambridge Phil. Trans., 6, p. 326. Ryan, Sibley Journal, 1904. C. E. Guye and H. Guye, Phys. Zeitsch., Jan. 15, 1906, p. 62.

[2] Rothé, Comptes Rendus, 147, p. 1279, 1908. Erickson, PHYS. REV., 27, p. 473, 1908. Laby and Kaye, Phil. Mag., 6, 16, p. 216, 1908.

[3] W. Wilson, Phil. Mag., 6, 17, p. 216.

[4] Tamm, Annalen, 6, p. 259, 1901.

[5] Ewers, Annalen, 17, p. 781, 1905.

of using for electrodes a point and plane, as practically all the workers have done previously, a fine wire and concentric cylinder were employed similar to the apparatus used by Almy.[1]

The luminous effect of the true point discharge is always confined to the point or its immediate neighborhood. This is a region of ionization in which ions of both signs are present. Those of the same sign as the point are repelled, pass out into the non-luminous portion and carry the current from the point to the other electrode, but it is generally assumed that their energy is too small to produce

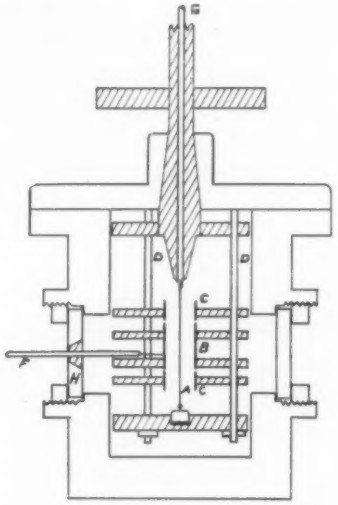

Fig. 1.

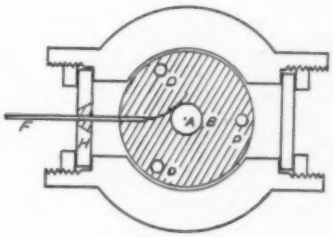

Fig. 2.

ions by collision. In the present work, the wire was covered uniformly with a blue glow when it was charged positively, but when negative in sign the discharge seemed to be localized in spots which were in constant motion. Between these spots could be seen a faint glow which covered more or less of the remainder of the wire.

Apparatus.

The arrangement of apparatus was comparatively simple. A carefully insulated wire was attached to one terminal of an influence machine whose other terminal was grounded. This wire formed one electrode and was placed in the center of a cylinder which

[1] Almy, Amer. J. Sci., 4, 12, p. 175, 1901.

formed the other, and which was connected to earth through a galvanometer that measured the leakage current. The form of the discharge chamber and the arrangement of the electrodes in it are given in Figs. 1 and 2, which show vertical and horizontal sections.

This chamber was made of brass with walls 1.3 cm. thick; the interior had a depth of 12 cm. and a diameter of 6.7 cm. It was closed with a cast-iron lid which was fastened to it by twelve bolts. Through this lid and carefully insulated from it passed a steel rod *G* and joined to this rod was the wire *A* which served as one of the electrodes. The cylindrical electrode *B*, 2 cm. long, was held in place by discs of hard rubber which were attached to the lid by the steel rods *D*. In order to obtain an uniform field two guard cylinders *C* were used. These were connected to the grounded walls of the chamber.[1] The insulated rod *F*, tipped with a german silver wire served as a connection between the cylinder *B* and the galvanometer.

The influence machine was the Toepler-Holtz type, electric-driven and provided with plates of mica three feet in diameter. It was capable of maintaining a difference of potential of approximately 100,000 volts and could furnish a current of at least 600 or 700 microamperes. The potential was regulated by means of a brush discharge occurring between the terminals of the machine and was measured by two Kelvin instruments, a vertical electrostatic voltmeter and an electrostatic balance whose respective ranges were from 1,000 to 16,000 and from 10,000 to 100,000 volts.[2] The gal-

[1] The actual distance between *C* and *B* seemed to have very little effect upon the current flowing, provided the gap between them was comparatively small. During the experiment no attempt was made to keep the distance uniform, but it was usually in the neighborhood of 0.02 cm.

[2] No accurate calibration of these instruments was attempted, but, as a check, the spark potential differences between spheres 2 cm. in diameter were determined for varying lengths. The results obtained by the two instruments, when plotted, gave a smooth curve with no discontinuity where the change was made. The results were then compared with those given by Heydweiller (Wied. Ann., 48, p. 220, 1893) and were found to be in fair agreement up to 26,000 volts. As far as this reading, the Kelvin instruments gave higher values with a maximum variation of 5 per cent. and an average of 3 per cent. For higher values, much lower results were obtained, but subsequent work made it quite certain that the instrument was more nearly correct than these readings showed, and the lack of agreement was probably due to a different arrangement of apparatus.

vanometer was of the d'Arsonval type, its maximum sensitiveness being 4.10^{-8} amperes per millimeter deflection for the scale distance employed. A shunt box was arranged so that currents up to 800 microamperes could be measured. The gas pressures were determined by a Schaeffer and Budenberg standard gauge, whose range was 100 atmospheres and it was not checked in any way. The instruments were grouped together in such a way that all the variables could be controlled and the readings taken by one observer.

Variations in the Discharge.

In reading over the literature of the subject, frequent references are made to the discordant results obtained, and how almost imperceptible changes in the conditions would cause most decided variations in the results, especially with the negative discharge. Naturally many such effects were met with in the course of the present work.

Size of Cylinders and Wire.—The first irregularity encountered was that due to the size of the cylinder and wire. With a phosphor-bronze wire, number 40, and a cylinder with an internal diameter of 0.8 cm., the currents obtained for various voltages did not follow any definite law and would not repeat themselves. When a wire of the same material but with a radius of 0.0018 cm. was used, the positive discharge gave concordant results, but the negative one was irregular. When a wire of supposedly the same diameter but made of platinum was introduced, both forms of discharge became regular, *i. e.*, if the values of the current and the corresponding differences of potential were plotted, a smooth curve was obtained. When the cylinder was replaced by another with a diameter of 1.59 cm., regular results were obtained even when the radii of the wires were varied from 0.037 to 0.001 cm.[1] A possible explanation of these results may be found in the work of Frank[2] who obtained

[1] The size of the wire seemed to have little effect upon the current-potential-difference curves, though, for small currents, the values arranged themselves according to the diameter, the smallest wire giving the greatest current. In passing from a number 40 wire to one having 0.037 cm. for a radius, there was a decided decrease throughout the entire range. Precht (Wied. Ann., 49, p. 150, 1893) found that, for small currents, the sharper the point the greater the current flowing, but for large currents all points had about the same effect.

[2] Frank, Wied. Ann., 21, p. 972, 1906.

evidence that ionization by collision was not confined to the immediate neighborhood of the point but occurred at some distance from it. He used a wire and cylinder whose radii were 0.005 and 0.7 cm. respectively and computed that with an electric field of 7,000 volts per centimeter the negative carriers would have suffcient energy to ionize air under atmospheric pressure at a distance of 0.64 cm. from the wire. The positive could do this only at a distance of 0.56 cm., even when the electric force was increased to 10,000 volts per cm. Thus, for the first cylinder employed in this work, the carriers, acted upon by 6,500 volts per cm., would probably reach the cylinder with sufficient energy to ionize the gas and thus change the form of the discharge. As can be seen in the case of the two wires which were supposedly of the same size but probably differed somewhat, it is evident that the dimensions of the apparatus had been unintentionally chosen so that the resulting discharge was on the boundary between a pure point discharge and some other form.

Temperature.—Readings obtained from day to day would rarely agree, and so some data were taken to see if different temperatures have any effect. The air in the room was cooled from 19° C. down to 13° C. and then allowed to warm slowly. Observations were made by keeping the machine at a constant voltage, and by taking the readings of the current for the different temperatures. One such series is given.

Positive Discharge. Potential Difference 4.14 *K.V.*

Temperature,	12°.3	13°.3	14°.9	17°.4	18°.5	19°.2 C.
Deflection of galvanometer,	6	5.83	5.75	5.86	5.75	5.75 cm.

This would indicate that the effect was very slight, if any, and that the increase in temperature caused a decrease in current.

This effect of temperature has been investigated more or less and the results show a decidedly complicated relation but, in most cases, the effect is small. Warburg[1] examined the discharge in oxygen and hydrogen at room temperatures and at 175° C. The presence of ozone complicated the former, but with the latter the current was slightly decreased with increase of temperature for the

[1] Warburg, Drude Ann., 2, p. 295, 1900.

negative discharge. The positive was affected only to a small extent; with small differences of potential, a decrease; with large differences, an increase, with rise in temperature. Ewers[1] found that apparently the only effect temperature has is to vary the value of the minimum potential. Thus if the differences between the actual potentials and the minimum potential are considered, temperature has no effect upon the current flowing. He states that the change in minimum potential depends upon a number of factors—gas used, its pressure, etc., and there seems to be no general relation. His range in temperature was from that of the room to that of liquid air. Pringsheim investigated the effect up to 600° C. and states that a change in temperature from 20° to 230° C. caused an increase in the negative discharge of about 10 per cent., and the positive discharge showed a similar change, though much smaller. From these results it seems certain that slight changes in the temperature of the gas could not be the cause of any decided variations.

Disruptive Discharge.—It was very early discovered that the potential which could be applied in the case of the positive discharge was limited for high pressures because values of potential were quickly reached which would cause the passage of a spark. On the other hand, no trouble of this kind occurred with the negative discharge. This effect is clearly seen in the following data:

Positive Discharge.

Pressure.	Potential Difference.	
37 Atm.	27.5 K.V.	Disruptive discharge.
29 "	24–25 "	" "
21 "	23 "	" "
12 "	24 "	No disruptive discharge.
9 "	33 "	" " "

Negative Discharge.

37 Atm.	30 K.	No disruptive discharge.
29 "	26 "	" " "

When the positive would stand such high potentials without a spark passing, as it did at 9 and 13 atmospheres, the point discharge was always well established and comparatively large cur-

[1] Loc. cit.

[2] Pringsheim, Annalen, 24, p. 145, 1907.

rents were flowing. The most plausible explanation of this is found in the ease with which the negative ions move. With the wire negative, the electrons would be repelled and, on account of their small inertia, would move rapidly away, leaving a preponderance of positive ions. Thus the decrease in the electric field would be even more abrupt than in the undisturbed state, and so the ionization would be limited to the neighborhood of the wire. This would aid in the establishing of the pure point discharge. In the case of the slow-moving positive ions, the effect would not be so pronounced and conditions similar to the ordinary spark discharge would arise.

Breaking of the Wire.—Considerable trouble was experienced in preventing the wire from breaking. This was due in part to the occasional passage of the disruptive discharge and also to the vibrations which the wire made when the current was passing. The vibrations were very rapid and seemed to be uniformly distributed in all planes. This tended to weaken the wire at its points of attachment. A wire large enough to eliminate these vibrations was tried, but it raised the potential necessary to give the required currents to such high values that it had to be discarded.[1] Finally platinum wire was used exclusively and was mounted by means of rings as shown in Fig. 1. If only moderate currents were allowed to flow, breakages were very infrequent.

Changes in the Surfaces of the Electrodes.—The cylinders were made of brass and, of course, tarnished somewhat after they had been in the discharge chamber for some time. Later they were silvered and then did not tarnish so quickly, but usually showed a mottled appearance. In three different cases, at atmospheric pressure, it was found that the polished cylinders gave values which were slightly lower than those given by the tarnished ones. Individual values could be found that would give the opposite of this, but when comparatively large currents were used and the discharge appeared to be normal, this result was obtained.

[1] Although the machine could furnish 100,000 volts, values much above 25,000 could not be used without remodeling the entire arrangement of apparatus because of the great leakage which occurred from all points of the system at these high potentials.

Fig. 3 gives a curve which shows the effect upon the discharge when the wire becomes corroded. In this case number 40 phosphor-bronze wire was used and when taken from the container was found to be covered by quite a thick layer of oxide which would obviously roughen the wire. Fig. 4 would indicate that the minimum potential was alone affected.

Source of Electricity.—Since the static machine furnished a constant current, it was thought that possibly the machine did not supply, at all times, sufficient current for the point discharge since the machine had to maintain as well a brush discharge used as a potential regulator. This was tested by placing a high resistance between the terminals of the machine and connecting the electrodes in parallel with a part of this resistance. Then the total current

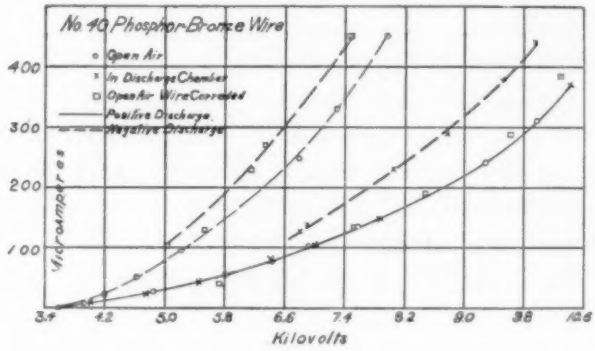

Fig. 3.

furnished by the machine was varied by changing the speed at which it was run. The maximum current used in the discharge chamber during this test was 50 microamperes and the total current furnished was varied from 150 to 300 microamperes without any effect upon the curves obtained. Consequently it is safe to conclude that the machine was capable of furnishing all the current that the discharge required. Pringsheim[1] found that the same variations were present whether he used a static machine or a high potential storage battery.

Discharge Chamber.—When the electrodes were introduced into

[1] Loc. cit.

the discharge chamber, the value of the current for a given difference of potential gradually fell for both forms of discharge. To see if this effect was due to the shielding of the electrodes, they were left in open air but were surrounded by a grounded cylinder of sheet iron, open at both ends. The current was the same as in open air. Similar results were obtained when the discharge took place in the chamber without the disc *H* (Fig. 1) in place. As soon as the chamber was completely closed, the decrease mentioned above appeared. If the disc were removed after the gas had carried the current for some time with the disc in place, values could be obtained which would lie between the two sets just described. The insulation of the rod *F* was tested and found to be good, so that could not be the reason for this variation.

It has been the experience of a number of experimenters who have worked with electrical discharges where it is necessary to enclose the electrodes, that similar phenomena frequently appear and no very good explanation could be given. Thus Tamm[1] and Zeleny[2] found that a glass vessel gave this effect most markedly, whereas vessels of cast iron or brass showed either no effect at all or else it was greatly diminished. Zeleny and Almy[3] overcame the difficulty by keeping fresh air circulating through the discharge chamber. Warburg[4] found that by a careful purifying of the gases these changes could be eliminated.

It was found that this effect could be observed with both positive and negative discharges, though occasionally the former would be unaffected as shown in Figs. 3 and 4. This would tend to indicate the effect of impurities, for ozone was always produced and it has a greater effect upon the negative than upon the positive discharge. Some attempt was made to find the dependence of this decay upon time and, as the effect was more noticeable at high pressures than at low, currents given by a definite potential at 28 atmospheres were observed every minute until a number of readings had been obtained. They did not seem to follow any definite law but gave

[1] Loc. cit.
[2] Zeleny, PHYS. REV., 25, p. 305.
[3] Loc. cit.
[4] Warburg, Drude Ann., 2, p. 295, 1900.

most irregular results, even occasionally increasing for a reading or two instead of decreasing. They apparently follow to a limited extent the form $i = Ke^{-at}$ but the variations were so great that it could not be said definitely that this law held.

The Gas.—The entire work was with air which was first passed through the purifiers of the liquid air machine and so contained very little carbon dioxide or water vapor, but some oil vapor may have been present. This air was stored under high pressure in a steel cylinder and a large quantity was obtained at one time. Thus, in taking most of the data during August the same air was used

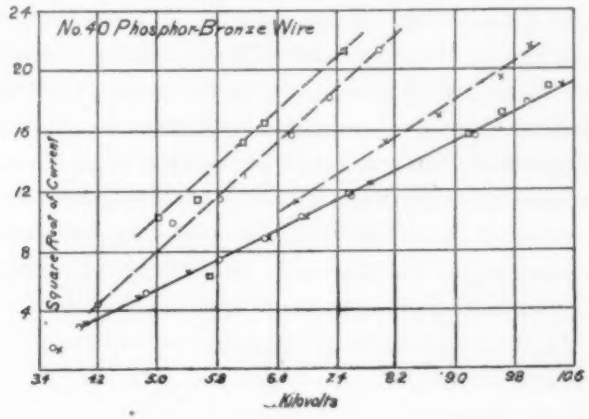

Fig. 4.

throughout, therefore the variations could not be due to the differences in the chemical constituents. A few runs were made with carbon dioxide, but it was found even more unsatisfactory than air.

When the gas was left in the chamber for several hours without a discharge passing, it was found that the current would be less than that obtained from fresh gas, but tended to increase as the discharge was allowed to continue. This could not be due to temperature change, for fresh gas and gas which had been in the container for about fifteen minutes gave identical results. After observing this an attempt was made to get consistent results by leaving the gas in the chamber for a number of hours but without success.

Possibly the room in which the experiments were carried on may have had something to do with the trouble, for it was in the basement and had no outside windows, though there were large doors on two sides of it which opened into light airy rooms and one of these doors was open constantly. Practically all the data were taken between April and August and most of the observations were made during July and August. It was found that if the discharge took place in the open air during the spring, fairly consistent results were obtained but, when the same thing was tried in the summer, nothing of any value resulted.

Some of these variations may be due to unstable conditions in the discharge itself. For example, Chattock[1] found that, in hydrogen, the values of the velocities differed among themselves by amounts so large that they could not be attributed to experimental errors. The same thing was noticed in air, but not to so great an extent. Evidently there are a number of factors which contribute to these variations, and this fact makes it difficult to say that a particular result is due to one of these factors and not to another. Thus the lessening of the discharge on July 27 was attributed to the polished surface of the cylinder. This explanation looks plausible; but, on the other hand, no explanation can be given for the sudden increase on August 12. Thus much of the preceding discussion can be considered only as plausible explanations rather than definite effects of specific causes.

RESULTS.

The work was almost entirely limited to finding the relation between current and impressed difference of potential, and curves of the form shown in Fig. 3 were always obtained. In Fig. 4 these same data are plotted with differences of potential as abscissæ and square roots of current as ordinates. The points determine more or less definitely a series of straight lines. This result is interesting, for Thomson[2] has developed, for the particular electrodes used in this work, an equation which would be represented by a similar

[1] Thomson, Conduction of Electricity through Gases, 2d ed., p. 504.

[2] Chattock, Phil. Mag., V., 48, p. 401, 1899. Chattock, Walker and Dixon, Phil. Mag., VI., 1, p. 79, 1901.

curve. It has been found that, at atmospheric pressure, this relation between current and difference of potential holds in almost every case. The exceptions are—for the negative discharge when out of the container, though the data in Fig. 4 follow this equation; also when a small static machine was used, in which case irregular results were obtained for the small currents used. As a result of the almost universal agreement, it is safe to say that Thomson's equation represents the general relation between current and potential difference when the current is larger than 10 microamperes, so in plotting the curves the square roots of the currents were always used as ordinates.

As the results for small currents did not fit the equation, the various approximations made in its development were investigated to see if they would have any effect. This departure is noticeable for currents of several microamperes and the terms neglected when such currents were used would introduce an error of less than 1 per cent.; hence their omission cannot explain the variation.

Thomson's complete equation is of the form

$$i = \frac{K}{2b^2}(V - V_0 - \alpha)^2.$$

k = the velocity of the ions under unit electric force.

a = radius of the wire.

b = radius of the cylinder.

V_0 = minimum potential difference for disruptive discharge.

$$\alpha = \tfrac{1}{2}\sqrt{C}\log\frac{2C}{\frac{i}{K}a^2}.$$

C is a constant of integration and cannot be larger than $i/K \cdot a^2$.

By assuming the critical spark length as 0.001 cm. and the maximum intensity as 100 electrostatic units, which is really less than its true value, the numerical values of the constants can be computed for the apparatus used. The two forms of discharge give the following:

$$i^{\frac{1}{2}} = 17.3(V - 1.43) \text{ positive.}$$

$$i^{\frac{1}{2}} = 20.5(V - 1.45) \text{ negative.}$$

α is a function of the current and thus varies considerably. In the positive discharge, for 0.1 microampere it is equal to 1.21; for 400 microamperes, it is 1.65. In the above equations, the average values are used. The experimental values of these constants were determined for three sets of curves obtained with the same sized wire and cylinder and are as follows:

$$i^{\frac{1}{2}} = 38.7(V - 8.72) \text{ positive.}$$

$$i^{\frac{1}{2}} = 45.7(V - 8.32) \text{ negative.}$$

$$i^{\frac{1}{2}} = 45.2(V - 8.28) \text{ negative.}$$

The agreement between the two sets is not good and the discrepancies are too great to be attributed to experimental errors. Of course the electric intensity used is lower than its true value, so possibly the agreement for α should be better than is indicated; but no error of that kind can account for the lack of agreement in the case of the other constant. This divergence may de due to lack of symmetry in the apparatus, so that the discharge might be concentrated along certain radii or radial planes instead of being uniformly distributed. The equation is also developed on the assumption of only one kind of ions being present in the non-luminous portion, while Wilson[1] and Campbell[2] in their work on the mass of these ions have shown that ions of both signs may be present.

The work of Frank[3] offers the best explanation for the variation in the slopes of the two sets of curves. He found that if the velocity of the ion due to unit electric intensity is determined in the neighborhood of the small electrode, the values varied most decidedly among themselves and were much larger than those determined by other workers. On the other hand, when he measured this quantity at some distance from the point, he obtained results in close agreement. This quantity is assumed a constant in Thomson's equation.

Figs. 5, 6, 7 and 8 show the effect upon the point discharge of an increase in gas pressure. The values plotted in Fig. 5 are the average of a number of runs with the wire charged negatively.

[1] C. T. R. Wilson, Phil. Trans., A, Vol. CXCII., p. 403, 1899.
[2] Campbell, Phil. Mag., 6, 6, p. 618, 1903.
[3] Loc. cit.

As was to be expected, the increase in pressure caused a great decrease in current, which might in part be attributed to the decrease

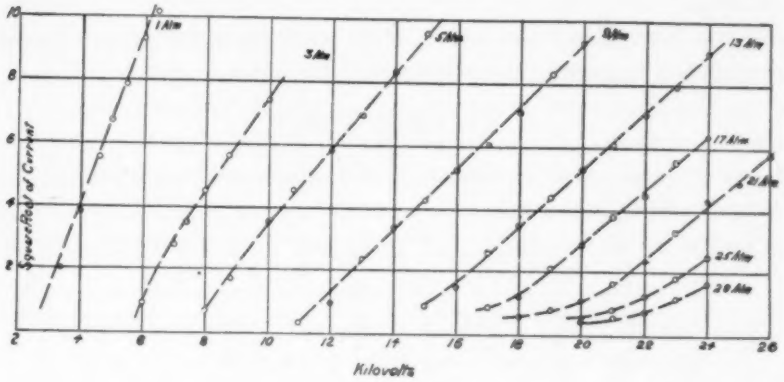

Fig. 5.

in velocity of the ions as shown by the change in the slope of the curves, and also to the much higher value of the minimum potential.

In Fig. 6 are plotted the values obtained with a phosphor-bronze wire using currents up to 400 microamperes. The irregularities

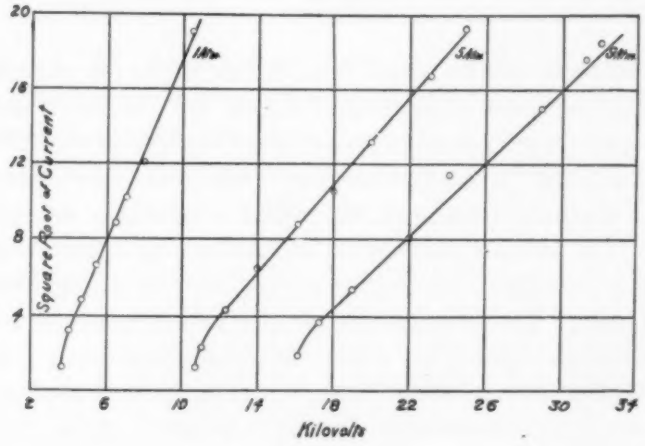

Fig. 6.

seen in the last two points on the curve at 9 atmospheres are probably due to inaccuracies in the voltmeter readings. These curves show very noticeably a variation from the straight line for values less

than 10 microamperes[1] and this same variation can be seen in curve 7 which indicates the effect of pressure upon both forms of discharge.[2]

It has been found that these small currents satisfy much better an equation suggested by Warburg of the form

$$i = AV(V - M).$$

A is a constant and M represents the minimum potential. Most observers have found that this equation seems to be followed quite generally when the point and plane are used as the electrodes.

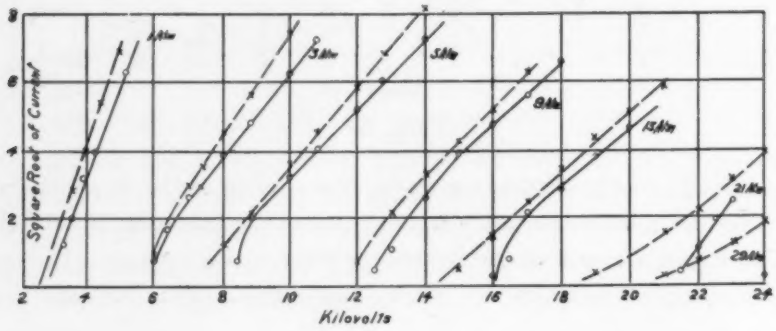

Fig. 7.

No explanation can be given why, in this work, the change from one equation to the other should appear for the small currents.

At a pressure of 17 atmospheres or more, the sign of this curvature reverses and the curves approach the X-axis more slowly than they should. This can be seen in Fig. 7, but is especially noticeable in Fig. 8. The data for this last set of curves were taken on August 12 and no reason is known for the unusual departure from the normal form. The general form of these curves is similar to those obtained when some agent is used to ionize a gas and the electric field between the electrodes is increased to such a strength that ionization by collision occurs. Hence it is natural to suppose that

[1] Curves of the same form have been obtained when the data published by other observers have been plotted with the square root of current as ordinates. Especially good examples were in the work of Tamm (loc. cit.), Zeleny (loc. cit.) and Sieveking (Ann., 1, p. 299, 1900) all of whom used the point and plane electrodes.

[2] In all the subsequent curves, the negative discharge will be represented by dotted lines and the positive, by full lines.

some other ionizing agent was present, which furnishes ions for these small currents and that the electric field had a very small part in producing them. This view is strengthened by the fact that pressures of 60 or 70 atmospheres could not entirely stop the negative current produced by a potential difference of 25,000 volts. The ions producing the current could hardly have been formed by collision, and the fact that it remained practically constant throughout wide ranges of pressures would indicate a saturation current.

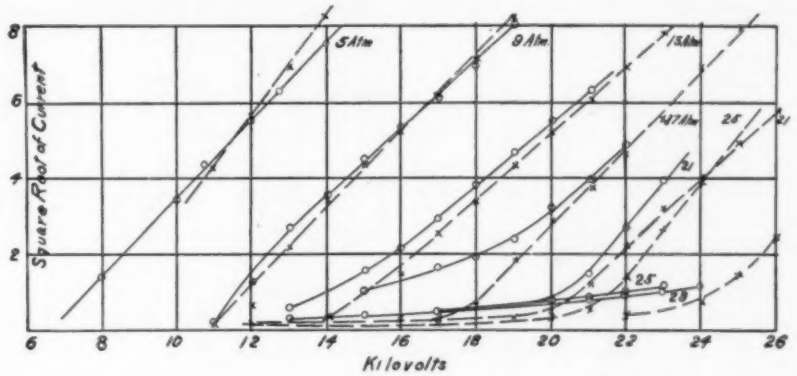

Fig. 8.

The work of Rothé and others mentioned in the early part of this paper would indicate that this effect should be more noticeable at high pressures than at low ones.

As a result of these curvatures, the minimum potential, which is characteristic of the point discharge, was not sharply defined. Other observers have usually found that the discharge began at a certain potential and then stopped at a lower one. They also mentioned that the current did not die away gradually but fell abruptly to zero. Most of them were working with galvanometers about 100 times as sensitive as the one used in this work; and the big influence machine did not work satisfactorily when run slowly enough to give the low potentials needed. Consequently none of these effects were noticed. At the high gas pressures it looks as though the minimum potential depends upon the sensitiveness of the galvanometer used, and if the true point discharge is concealed by some other discharge, then the minimum potential can have but little significance.

According to Thomson's equation, the ratio of the slopes of the curves for the different discharges should be the square root of the velocities of the two kinds of ions. Trying this for the constants in the equations given on page 732, they give as the ratio 1.37, whereas Chattock found it to be 1.36. This close agreement is a matter of chance, for other curves give values varying from 1.22 to 1.48. Though two cylinders of unequal size were used, it was impossible to see if the slopes of the lines varied inversely as the radii because the results with the small cylinder were so irregular.

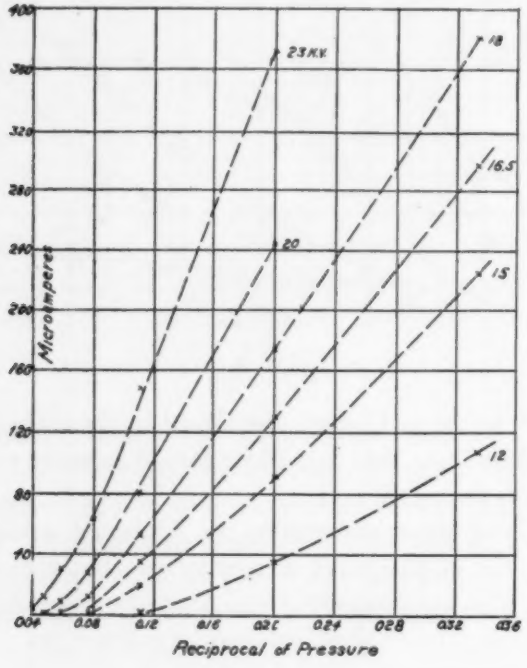

Fig. 9.

If the assumption is made that the velocity of the ions is inversely proportional to the gas pressure, then certain relations may be deduced from the equation. Thus if the voltage is kept constant, then the current must vary inversely with the pressure. This holds for large currents and rather high voltages, as shown in Fig. 9. To obtain this curve, the lines in Fig. 5 had to be exterpolated, but no values greater than 400 microamperes were used, and Fig. 6

shows that the point discharge still holds for that current. In a similar way the equation says that, for constant current, the voltage must increase as the square root of the pressure and Figs. 10 and 11

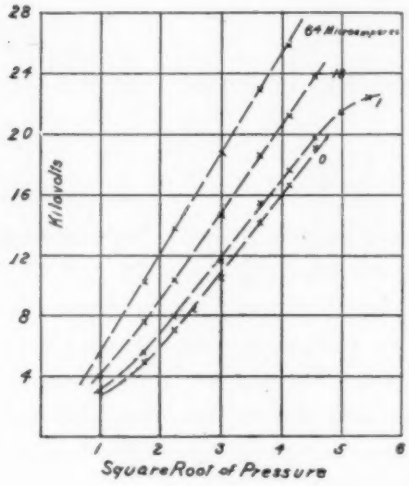

Fig. 10.

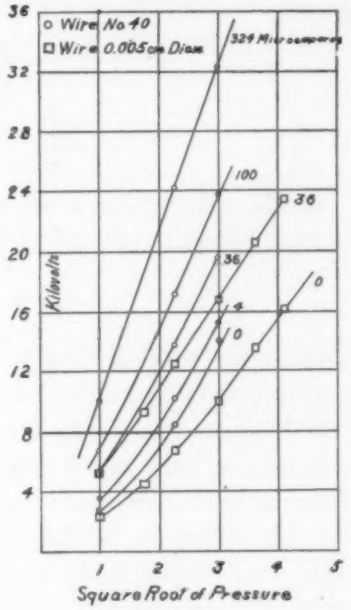

Fig. 11.

show that this condition is satisfied for large currents. Fig. 11 also indicates that the size of the wire has a very decided effect upon these curves. These figures tend to confirm the idea that the velocity of the ions vary inversely as the pressure.

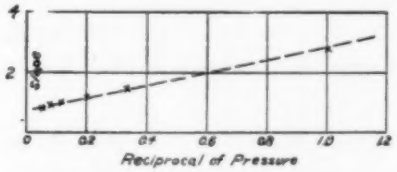

Fig. 12.

If the slopes of the lines given in Fig. 5 are plotted as ordinates and the reciprocals of pressure as abscissæ, a straight line results as shown in Fig. 12. According to Thomson's equation, this would mean that the velocity varies inversely as the square of the pressure,

which is antagonistic to the results given in Figs. 9, 10 and 11, but it is in approximate agreement with Tamm's[1] work, for he found that the following equation held for pressures less than one atmosphere:

$$i_x = i_{76}\left\{\frac{76}{x} - \sqrt[3]{\frac{v}{10^5}}\log\frac{76}{x}\right\}^2.$$

CONCLUSIONS.

1. The relation between current and impressed potential difference follows the equation

$$i^{\frac{1}{2}} = A(V - M)$$

for currents varying from 10 to 400 microamperes. For currents less than 10 microamperes, the results are irregular.

2. Pressure has a very great influence upon the true point discharge, due both to an increase in minimum potential and to a decrease in the velocity of the ions. The curves would indicate that the velocities of the positive and the negative ions become more nearly equal at high pressures, due probably to the loading down of the electron by neutral molecules.

3. It was found that the slopes of these straight lines vary inversely as the gas pressure; that, for a given current, the corresponding voltages vary as the square root of the pressures; that the current given by a constant difference of potential vary inversely as the pressure. These last two relations support the view that the velocity of the ions decrease directly as the pressure, while the first one indicates that the velocity varies inversely as the square of the pressure. From the present work there is no means of telling which is the correct relation.

4. These relationships were found to hold up to 17 atmospheres, but above that currents large enough could not be obtained by the present arrangement of apparatus to test them.

5. At the high pressures, phenomena were observed which might be explained by the presence of an ionizing agent, other than the electric field, which tended to mask the true point discharge.

[1] Loc. cit.

The experimental work was done in the Physical Laboratory of Cornell University during the spring and summer of 1907. The author wishes to express his appreciation of the advice and suggestions offered by the various members of the department, especially Professors Merritt and Shearer.

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PHYSICAL PROPERTIES OF BINARY LIQUID MIXTURES.

BY J. C. HUBBARD.

INTRODUCTION.

THE study of a solution, a salt in water, for example, is in general, complicated by electrolytic dissociation, and by the probable formation of hydrates. These two effects may more or less effectually mask other effects, which, if they exist, would cause apparent deviations from a theory of solutions which takes only the two mentioned into account. There are, however, certain binary liquid mixtures the physical properties of which present such simple and small deviations from the properties of the pure substances added together, that it may be hoped by an investigation of them to be able to trace minutely the condition of each component in the mixture, thereby gaining new insight into some of the second order effects in solutions and also, possibly, learning something of the mechanism of the liquid state itself.

For the study here summarized are chosen such simple properties as could be measured with great precision, as density and index of refraction; and, in order to secure as wide a basis of comparison as possible, it seemed best to choose for study those pairs of liquids for which the partial and total vapor pressures have already been so carefully investigated by Zawidzki.[1]

The specific volumes are given for the temperatures at which he measured the vapor pressures. In addition are given the specific volumes at 25° C. and the indices of refraction at the same temperature for the lines C, D, F and G', thus securing data for determining the mean temperature coefficient of expansion, and for the dispersion. It is unfortunate that the indices of refraction could not also have

[1] J. von Zawidzki, Über die Dampfdrucke binärer Flussigkeitsgemische, Zs. phys. Chem., 35, p. 129, 1900. See also Rosanoff and Easley, Amer. Chem. Soc. Jour., XXXI., No. 9, p. 953, 1909; Zs. für phys. Chem., p. 641, 1910.

been measured for the same temperature as the vapor pressures, but, on account of the great volatility of most of the substances, it was found that such determinations required facilities not available.

The methods of obtaining results such as are given here call for nothing original in principle, but it is hoped that the procedure evolved has produced results of greater accuracy than hitherto obtained for such mixtures.

Apparatus.

On account of the excessive volatility of the substances studied, and of the difference, in general, of composition of liquid and vapor, it is very difficult to prevent changes of composition through evaporation. Each point of the procedure was carefully examined, and the process was finally reduced to a certain rigid, mechanical routine, which, though arbitrarily varied in detail, is capable of giving results usually reproducible to from two to five parts in one hundred thousand, depending upon the volatility of the substances.

After much preliminary work in measuring specific volumes, involving a trial of specially designed pyknometers, it was found that the most reliable results were to be secured by the use of the common specific gravity bottle with graduated neck and solid glass stopper. The bottles were each of 10 c.c. capacity; the necks were about 4 cm. in length, graduated in millimeters and of about 1.5 mm. internal diameter. The glass stoppers were ground until no loss by evaporation of any of the liquids contained in the bottles could be detected in an interval of several hours. The volume of each bottle was calibrated for about twenty points along the scale at both temperatures at which the density was to be measured. It was found that where the temperature changes to which the bottles were subjected varied in a regular cycle the calibration values could always be reproduced to 2×10^{-4} cm.^{3}, or to two parts in one hundred thousand of the capacity of the bottle. When the bottle was to be used at a new temperature it was recalibrated. Much of interest came of the calibration of these bottles. The calibration curves finally settled down into a state very nearly independent of temperature changes between 0° and 60° C.

Two thermostats, each of five gallons capacity, regulated and heated electrically, were used in connection with the specific volume

measurements. One of these was kept at 25°.00 ± .002 C. throughout the series, and the other at either 35°.17 ± .001 or 50° ± .001 to agree with Zawidzki's temperatures as the case required. The thermometers read to .001° and were compared from time to time with a standard (Baudin, calibrated at the International Bureau of Weights and Measures) loaned by Professor Webster.

The pyknometer bulbs were held in the thermostats by means of wire stages. The stopper, with a few millimeters of neck of a bulb, was allowed to protrude from the water, and over this was placed a heating coil which kept the stopper and the upper part of the neck several degrees warmer than the water in the thermostat. This was found necessary to prevent the condensation of liquid mixture in the top part of the neck, causing a lowering in the meniscus reading of the pyknometer. The mensicus reading was made by means of a mirror held below the surface of the water, obviating the necessity of disturbing the heating coil about the neck of the bulb.

From the thermostat at 25° was led a stream of water through thick walled, jacketed tubing for the temperature regulation of the Pulfrich refractometer (new construction) which was used in the measurement of the indices of refraction. The room being at about 20° made necessary a small amount of heating to compensate the slight loss by radiation. This was accomplished by passing the tubing through the core of a small rheostat which could be warmed any desired amount. By this arrangement the refractometer could be kept at 25° C. without sensible deviation. The thermometer scale of the refractometer reads to .01° C.

Preparing Volatile Mixtures of Known Composition.

The largest error, and the one most difficult of estimation, is to be found in the determination of the composition of the mixture. As this subject seems to have received very little attention it may be worth while to enter into it here, the object being to show that large systematic errors may be produced unless proper precautions are taken.

In the first place, all weighings must be reduced to vacuo, otherwise there will be a systematic error in the "per cent. composition,"

amounting in some cases to 0.1 per cent, due to the difference of density of the two components.

A quantity a of liquid A is first weighed out in the weighing bottle, then a quantity b of the second liquid B is poured into the bottle and the total amount, $a + b$, is determined. The proportion of A in the mixture is then supposed to be $z = a/(a + b)$. If a series of observations be obtained, say of the deviation from the additive law of specific volume for the mixture $A - B$, as

$$\Delta v = v - v_C = v - [zv_A + (1 - z)v_B]$$

(where v is the observed, and v_C the calculated specific volume), z being determined as described above, a smooth curve for Δv and z may be obtained. If, now, a second series of observations be made, always weighing out first the liquid B, a smooth curve is again obtained, but this curve will not coincide with the first. The discrepancy is caused by the evaporation of the first liquid when the cover of the weighing bottle is removed to add the second liquid. The numerator of the composition fraction for the liquid first weighed out will be too large.

The error due to this cause may be brought down to the other errors of the determination by subtracting from the weight of the first component a quantity determined by many trials as a suitable evaporation correction. This number is obtained by placing a quantity of the liquid A, for example, in the weighing bottle and making repeated weighings, between each weighing removing the stopper in the same manner and for the same length of time (five seconds) as was done when actually making up the mixture. The amount of evaporation so measured is surprisingly constant. Let it be Δa; then, instead of $z = a/(a + b)$, we have $z' = (a - \Delta a)/w$ where w is the total weight. In these experiments a had values from 6 in a very few cases to 60 gr., and Δa varied from .0006 gr. in the case of acetic acid to .018 gr. in the case of carbon disulphide; the calculated fraction z thus having a correction of from 1 in 10^5 to 1 in 300, usually however about 1 in 10^4. When the correction is applied the above mentioned discrepancy disappears.

One example is given here (Table I., Fig. 1) to show the manner of applying the evaporation correction.

TABLE I.[1]

Evaporation Correction for Carbon Disulphide-Methylal. 25° C.

Δa (CS_2) = .018 ± .001 *gr.* v_1 (CS_2) = .79621.
Δb (*Meth.*) = .017 ± .001 *gr.* v_2 (*Meth.*) = 1.17233.

Wt. CS_2	Wt. Meth.	Total.	% CS_2	Δv	% Corr.	Corr. to Δv.
	11.318	12.978	12.793	.00525	+.128	+.00049
	10.001	13.999	28.560	993	+.122	+ 43
	8.963	14.525	38.290	1129	+.118	+ 45
6.506		14.885	43.708	1248	−.120	− 45
	8.029	14.736	45.513	1188	+.117	+ 44
	7.187	15.300	53.026	1179	+.113	+ 41
	6.224	15.531	59.92	1130	+.110	+ 43
	6.024	15.892	61.12	1097	+.109	+ 41
9.862		15.781	62.493	1189	−.113	− 42
10.542		16.126	65.371	1157	−.109	− 41
12.544		16.670	75.251	966	−.110	− 42
15.087		17.431	86.553	632	−.104	− 38

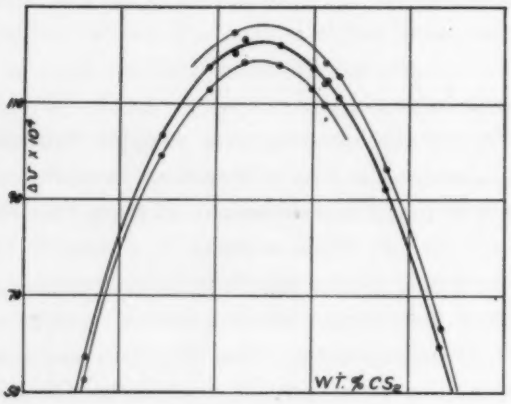

Fig. 1.

This case represents the greatest extreme, both in volatility and in the small quantity of liquid used, giving by far the largest corrections obtained in any of the results.

The sixth column of the table shows the corrections obtained for the percentage composition, while the last column gives the corresponding corrections to Δv. When the carbon disulphide is weighed

[1] For complete data see Table II. All the weights given in the table were made to 0.1 mmg. but as the evaporation correction could not be determined so accurately the weights are given only to the nearest milligram. All weights reduced to vacuo.

out first the percentage number is too great, and since the specific volume of CS_2 is smaller than that of methylal the calculated volume is too small, making the deviations of the specific volume from the additive law too large. The reverse is true when methylal is first weighed out; the deviations are too small. It will be seen that two curves are obtained which are brought together into one (the heavy curve of the figure) when the corrections are applied. The consideration of these systematic errors, due to errors in the percentage composition, applies, not only to densities, but to all other properties as well, and it is unfortunate that so little care has thus far been bestowed upon it.

Operation.

When a given mixture has been made up it must be thoroughly shaken, and this must be done without wetting the space between the rim and the stopper of the weighing bottle, in order to insure all of each component being present. (Much time was lost in the beginning in locating errors finally found to be due to imperfect mixing, or to the loss of liquid in the rim space before mixing had become complete.) The stopper is then quickly removed, about 15 c.c. of the mixture is withdrawn by gentle suction from the bottom of the bottle into a slender stemmed pipette of just sufficient capacity. The pipette tube is then inserted into the pyknometer bulb to the bottom and the mixture is forced out gently until the bottle is full. Some of the liquid is allowed to run over; about 3 c.c. are left in the transferring tube. This procedure insures that very little of the liquid now in the pyknometer has been exposed to air, and until it was adopted it was found impossible to get concordant results. Some of the liquid is next removed from the graduated neck by inserting a capillary tube connected to a suction pump, and the exposed interior of the neck is dried. The stopper is inserted, and the bulb is placed in position in the thermostat at the lower temperature. When the meniscus reading has become constant the bulb and contents are weighed, more liquid is removed from the neck, as before, and the bulb is placed in the thermostat at the higher temperature, when similar observations are made. These observations give the specific volumes at the two temperatures.

The mixture is next brought to the refractometer temperature by placing the bulb in the first thermostat, after which three successive samples are taken from the bottom of the bulb for the determination of the indices of refraction with the sodium and three principal hydrogen lines. About 90 minutes are necessary for the completion of all the observations of a mixture of given composition.

THE "ADDITIVE LAWS." NOTATION.

Vapor Pressure.—When the vapor pressure of pairs of liquids are plotted against the molecular proportion of one of the components, three types of curves are obtained. The simplest is a straight line, such as would be expected if the components exerted neither physical nor chemical influence on each other, but mixed in all proportions. Besides this curve are curves convex toward the axis, and curves concave toward the axis. The former are conceivably caused by a lessening of the number of evaporating molecules, on account of a union or by increased cohesion; the latter by an increased number of evaporating molecules, possibly caused by dissociation of polymerized molecules, or by a lessening of cohesion due to the mixing.[1] In any case the deviation from the straight line serves as a valuable criterion for the classification of binary mixtures, and, taken in connection with the deviation of other properties, may be expected to throw some light on the theory.

We shall consider the deviations from the simple additive law.

$$p_c = xp_1 + (1 - x)p_2,$$

where x is the number of mols of A in one mol of mixture, p_1 and p_2 being the respective vapor pressures of A and B in the pure state.

$$\Delta p = p - p_c, \qquad (1)$$

where p is the observed total pressure.

Specific Volume.—Let v_1 and v_2 be the respective specific volumes of the substances A and B, and v_c the calculated specific volume of the mixture, and let w_1 and w_2 be the weights of the two substances in the mixture. Then, assuming that there is no change

[1] See Zawidzki, loc. cit., p. 157 et seq.; also Ostwald, Allg. Chemie, II., p. 617; Dolezalek, Zeit. f. phys. Chem., 64, p. 727, 1908.

of volume on mixing, the total calculated volume is

$$V_c = w_1 v_1 + w_2 v_2 = (w_1 + w_2) v_c$$

whence

$$v_c = z v_1 + (1 - z) v_2$$

where z is the weight of A in one gram of the mixture. If v is the observed specific volume of the mixture then

$$\Delta v = v - v_c \tag{2}$$

gives the deviation of the volume from the additive law.

Indices of Refraction.—The theory of dispersion for liquids is not as yet in a satisfactory state. The most common expression for the refractivity $R = N/d = (n^2 - 1)/(n^2 + 2)d$ (Lorenz-Lorentz), has strong theoretical support, and preserves a fair constancy even for change of state. Planck's theory gives the same expression with the assumption of a single absorption band for the substance, but does not lead to a simple expression for the refractivity when there is more than one absorption band.[1]

The well-known additive law

$$R_c = z R_1 + (1 - z) R_2, \tag{3}$$

where z is the weight of A per gram of the mixture, has been experimentally studied by a great number of observers, usually without much question as to whether the liquids investigated followed the dispersion formulæ. As, however, deviations from (3) tend to show the need, and perhaps indicate the direction, of further investigations both into the theory of dispersion and into the dispersion of particular liquids, such work has a distinct value.

The deviation of refractivity is

$$\Delta R = R - R_c. \tag{4}$$

If we multiply (3) by d_c, the calculated density, remembering that $R = N/d$, we have

$$N_c = y N_1 + (1 - y) N_2, \tag{5}$$

y being the volume of A in 1 c.c. of mixture.

[1] On the dispersion of liquids see also A. Trowbridge, PHYS. REV., XXVIII., p. 389, 1909.

Pulfrich gives the empirical equation

$$\frac{N - N_e}{N} = \alpha \frac{d - d_e}{d} = \alpha c = \alpha \frac{v_e - v}{v_e}, \tag{6}$$

or

$$\alpha = -\frac{\Delta N}{N} \Big/ \frac{\Delta v}{v_e}, \tag{7}$$

in which α is supposed to be constant, and $N = (n^2 - 1)/(n^2 + 2)$. Eq. (6) leads to the expression

$$R \frac{1 - \alpha c}{1 - c} = R_e = zR_1 + (1 - z)R_2,$$

which is Pulfrich's modification of the additive law.[2] We also have from (6)

$$\Delta R = (\alpha - 1)(v_e - v)\, N = -(\alpha - 1)\, N \Delta v. \tag{8}$$

In the following tables the values of α are calculated from (7), and ΔR from (8) except in two cases, where Δv being too small, ΔR is calculated from (4).

THE SUBSTANCES.

The substances benzol, ethyl acetate, ethyl iodide, carbon tetrachloride, acetic acid, chloroform, acetone, methylal and carbon disulphide were generously furnished by the Department of Chemistry of Clark University, and I am indebted to Mr. C. W. Bacon, a graduate student of that department, for carrying out their purification. It was obviously important to have had the substances in a state of high purity. The methods of purification, as carried out by Mr. Bacon, will be given in connection with each substance.

RESULTS.

In the case of each mixture are given three tables. In the first table of each set, besides the proportions by weight of one of the substances, are given in order the values of v_{25} and $v_{35.17}$, or v_{50} as the case may be, and n_C, n_D, n_F and $n_{G'}$. In the second table are given the deviations of specific volume Δv_{25}, $\Delta v_{35.17}$ or Δv_{50}, and the deviation of refractivity for the D line, ΔR_D, beside the constants

[2] Pulfrich, Zeit. f. phys. Chem., 4, 561, 1889; see also Winkelmann, Handbuch, 6, p. 650.

α, of the Pulfrich equation, for each of the wave-lengths. In the last table of each set are given the molecular and weight proportions of the mixtures and the total vapor pressures as given by Zawidzki (*loc. cit.*), and the deviation Δp of these total pressures from the simple additive law. Finally for each set of results has been drawn a figure showing the deviations of pressure, specific volume and refractivity plotted as functions of the weight composition of the mixture.

I. *Carbon Disulphide—Methylal.*

The carbon disulphide was washed with 5 per cent. sodium hydroxide solution and set away over quicklime for twenty-four hours being occasionally shaken. It was then poured into a bottle containing mercury and shaken frequently until the disagreeable odor had disappeared, decanted from mercury and distilled.

The fraction was collected boiling within 0°.2 C.

The methylal was dried with $CaCl_2$ and distilled over within a small fraction of a degree. The sample chosen came over within 0°.2 C.

The evaporation correction for CS_2 is .018 ± .001 gr. and for methylal .017 ± .001 gr. The total amount of mixture was about 15 gr.; thus the error in the weight composition is about 7×10^{-5}.

Remarks on Tables II., III. and IV.—This was the first set of observations completed, and as the temperature regulation of the refractometer had not been made perfect, readings for the same samples varied as much as 2′, which corresponds to about 2 units in the fourth decimal place of the index of refraction. As every determination in the table is a mean of at least three, the probable error is considerably less. The asterisk (*) after specific volume determinations indicates a slight amount of boiling in the pyknometer during the measurement at the higher temperature. The disturbance affected the meniscus to the extent of 1 division, introducing an uncertainty of 3 in 10^{-4} in the four results marked. The other volume errors are subject to the reading errors already mentioned of 2×10^{-5}. The composition error of 7×10^{-5} produces uncertainty in the values of v of 3×10^{-5}.

The value of α diminishes with the amount of CS_2 present, and with diminishing wave-length.

TABLE II.

Carbon Disulphide—Methylal.

No.	x(wt)CS_2	v_{25}	$v_{35.17}$	n_C	n_D	n_F	$n_{G'}$
	0.00000	[1.17233]	1.19043	1.34850	1.35018	1.35425	1.35759
	0.00000	1.17214	1.19044	1.34845	1.35018	1.35420	1.35759
	0.00000	1.17216	1.19043	1.34916	1.35078	1.35489	1.35832
	Mean.	1.17215	1.19043	1.34870	1.35038	1.35444	1.35783
1	.12921	1.12932	1.14685	1.36939	1.37164	1.37730	1.38206
2	.28682	1.07469	1.09108	1.39871	1.40178	1.40954	1.41639
3	.38408	1.03949	1.05500*	1.41928	1.42294	1.43220	1.44037
4	.43588	1.02031	1.03538	1.43107	1.43502	1.44524	1.45440
5	.45630	1.01293	1.02807	1.43595	1.44005	1.45054	1.45986
6	.53139	.98458	.99905	1.45459	1.45922	1.47115	1.48179
7	.60034	.95819	.97243*	1.47286	1.47810	1.49146	1.50325
8	.62226	.94959	.96319*	1.47937	1.48471	1.49857	1.51091
9	.62380	.94911	.96265	1.47964	1.48497	1.49889	1.51123
10	.65262	.93797	.95114*	1.48798	1.49357	1.50815	1.52061
11	.75141	.89891	.91140	1.51859	1.52508	1.54205	———
12	.86449	.85309	.86443	1.55901	1.56665	1.58690	1.60505
	1.00000	.79620	.80611				
	1.00000	.79623	.80611				
	1.00000	.79621	.80609				
	Mean.	.79621	.80610	1.61440[1]	1.62357	1.64830	1.67073

[1] It was impossible to get accurate readings for CS_2 in the refractometer. The values are reduced from Landolt & Börnstein's tables.

TABLE III.

Carbon Disulphide—Methylal.

No.	Δv_{25}	$\Delta v_{35.17}$	ΔR_{D25}	a_C	a_D	a_F	$a_{G'}$
1	.00574	.00607	.00030	.773	.767	.734	.742
2	1036	1088	91	.650	.638	.630	.566
3	1174	1219	126	.595	.579	.574	.561
4	1203	1248	136	.576	.565	.545	.503
5	1232	1301	151	.548	.534	.529	.515
6	1220	1285	166	.519	.503	.492	.472
7	1173	1273	170	.518	.488	.472	.472
8	1138	1189	161	.463	.444	.425	.410
9	1147	1196	175	.483	.467	.449	.432
10	1116	1152	179	.469	.448	.424	.475
11	924	976	163	.452	.425	.400	—
12	594	626	143	.293	.261	.221	.204

TABLE IV.

Carbon Disulphide—Methylal (Zawidzki). 35°.17 C.

x and x CS_2	$p_{35.17}$	Δp	x and x CS_2	$p_{35.17}$	Δp
0.0000	587.7	0.0	.6060	695.5	152.1
.0496	613.3	29.2	.6803	685.4	147.5
.1044	638.9	58.9	.7353	675.4	141.5
.1651	660.1	84.5	.7927	661.6	132.0
.2719	686.0	118.2	.8421	644.6	118.5
.3480	696.7	134.5	.8573	634.7	109.7
.3904	700.4	141.2	.9130	603.2	82.4
.4542	703.2	148.7	.9576	564.2	46.6
.4942	701.4	149.8	1.0000	514.5	0.0
.5377	700.3	152.0			

The values of $\Delta p_{35.17}$, Δv_{25}, $\Delta v_{35.17}$ and ΔR_{D25} are plotted in Fig. 2.

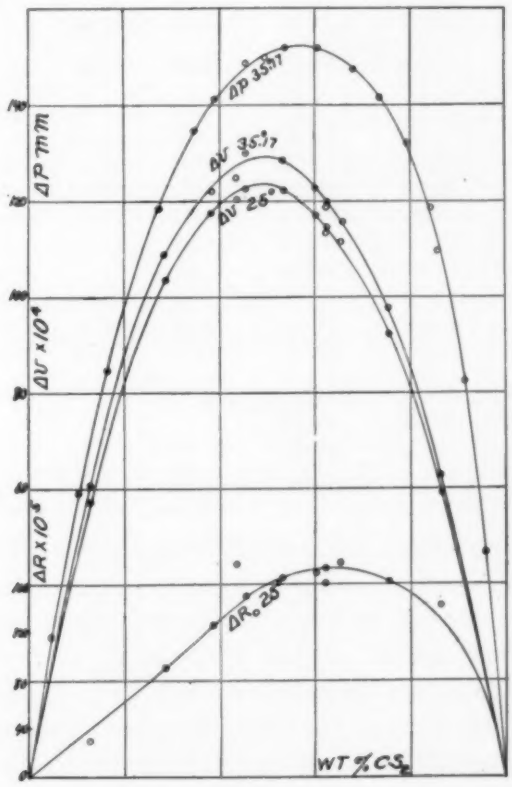

Fig. 2.

II. *Carbon Disulphide—Acetone.*

The same CS_2 was used as in the last case. The acetone was mixed with 6 per cent. solid $KMnO_4$, boiled in a reflux condenser over a water bath for three hours, distilled off rapidly, dried over freshly ignited K_2CO_3 and distilled in the usual manner. Boiled at 56°.0 to 56°.3 C.

Evaporation correction for CS_2 = .018 ± .001 gr.; for acetone, .010 ± .001 gr. Corresponding probable error in the weight composition is 7×10^{-5}.

TABLE V.

Carbon Disulphide—Acetone.

No.	z(wt)CS_2.	v_{25}	$v_{25.17}$	n_C	n_D	n_F	$n_{G'}$
	0.00000	[1.26913]	[1.28810]	1.35450	1.35636	1.36112	1.36509
	0.00000	1.26906	1.28824	1.35450	1.35636	1.36112	1.36509
	0.00000	1.26903	1.28821	1.35475	1.35662	1.36140	1.36540
	Mean.	1.26905	1.28823	1.35458	1.35645	1.36121	1.36519
1	.13245	1.21357	1.23204	1.37333	1.37576	1.38177	1.38701
2	.29326	1.14319	1.16040	1.40047	1.40364	1.41171	1.41887
3	.40329	1.09304	1.10938	1.42182	1.42567	1.43533	1.44390
4	.51761	1.03962	1.05502	1.44776	1.45253	1.46387	1.47471
5	.51799	1.03937	1.05478	1.44794	1.45253	1.46417	1.47522
6	.51902	1.03847	1.05389	1.44819	1.45271	1.46439	1.47471
7	.64733	.97694	.99106	———	———	———	———
8	.71137	.94547	.95867	1.50093	1.50692	1.52263	1.53661
9	.83283	.88407	.89605	1.54325	1.55043	1.56942	1.58644
10	.86892	.86551	.87711	1.55702	1.56465	1.58477	1.60291
	1.00000	.79620	[.80590]				
	1.00000	.79623	.80609				
	1.00000	.79619	.80611				
	Mean.	.79621	.80610	1.61440	1.62357	1.64830	1.67073

Remarks on Tables V., VI. and VII.—Owing to the uncertainty of the evaporation correction to .001 gr. the compositions z (V., VI.) are again subject to an error of 7×10^{-5} which makes the calculated volumes and Δv subject to an error of 3×10^{-5}. The observed volumes are measured to 2×10^{-5}. The indices are measured to the errors of the instrument (see "Operation"). The values of the deviations are plotted with the proportions by weight in Fig. 3.

III. *Chloroform — Acetone.*

The acetone was purified as in the previous case. The chloroform was shaken with 5 per cent. NaOH solution, separated and shaken

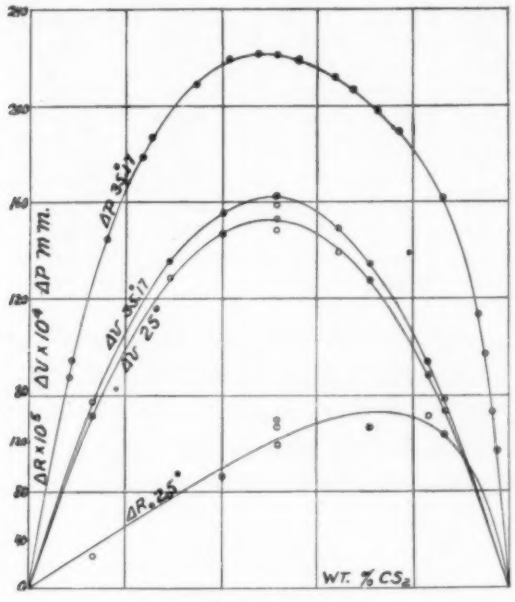

Fig. 3.

three times with distilled water. It was next dried over $CaCl_2$ for twenty-four hours, filtered and distilled. The distillate smelled

TABLE VI.

Carbon Disulphide—Acetone.

No.	Δv_{25}	$\Delta v_{35.17}$	ΔR_{D25}	a_C	a_D	a_F	$a_{G'}$
1	.00715	.00767	.00027	.855	.836	.895	.899
2	1280	1356	77	.762	.755	.766	.747
3	1469	1559	92	.779	.755	.764	.755
4	1531	1633	140	.710	.662	.698	.626
5	1525	1628	133	.700	.676	.675	.579
6	1483	1589	118	.720	.705	.700	.696
7	1397	1493	—	—	—	—	—
8	1278	1341	133	.666	.650	.640	.637
9	881	936	141	.516	.497	.485	.479
10	732	781	124	.508	.477	.458	.438

TABLE VII.

Carbon Disulphide—Aceton (Zawidzki). 35°.17 C.

$x CS_2$	$s CS_2$	$\rho_{35.17}$	$\Delta\rho$	$x CS_2$	$s CS_2$	$\rho_{35.17}$	$\Delta\rho$
0.0000	0.0000	343.8	0.0	.5716	.6363	652.2	212.1
0.0624	.0802	441.7	87.4	.6144	.6760	653.7	206.4
.0690	.0885	449.6	94.2	.6713	.7278	655.0	198.1
.1271	.1602	510.0	144.8	.7208	.7720	654.6	189.4
.1857	.2323	553.8	178.7	.8280	.8630	645.1	161.8
.2038	.2511	564.9	186.8	.9216	.9391	612.2	113.1
.2815	.3392	600.7	209.5	.9378	.9520	598.4	96.6
.3526	.4165	622.8	219.6	.9584	.9679	578.1	72.8
.4100	.4766	634.6	221.7	.9692	.9764	564.0	56.9
.4502	.5176	641.2	221.5	1.0000	1.0000	512.3	0.0
.4953	.5625	646.1	218.9				

strongly of phosphine and also gave the test for chlorine. The whole material was then shaken up with NaOH, washed with water and dried as before. It gave no test for chlorine and after filtration was used without further distillation. Boiling point 61°.2 C. Evaporation corrections: Chloroform, .015 ± .001 gr.; acetone, .010 ± .001 gr.

TABLE VIII.

Chloroform—Acetone.

No.	s Chl	v_{25}	$v_{35.17}$	n_C	n_D	n_F	$n_{G'}$
	0.00000	1.27403	1.29334	1.35436	1.35620	1.36096	1.36495
	0.00000	1.27401	1.29330	1.35436	1.35621	1.36087	1.36483
	0.00000	1.27402	1.29325	1.35434	1.35621	1.36091	1.36474
	Mean.	1.27402	1.29330	1.35435	1.35621	1.36091	1.36484
1	.16664	1.17445	1.19201	1.36261	1.36454	1.36941	1.37344
2	.33039	1.07637	1.09208	1.37211	1.37417	1.37920	1.38334
3	.45832	.99950	1.01378	1.38122	1.38332	1.38848	1.39275
4	.56298	.93643	.94957	1.38982	1.39196	1.39728	1.40171
5	.64507	.88682	.89911	1.39721	1.39943	1.40494	1.40949
6	.72276	.83976	.85122	1.40531	1.40757	1.41319	1.41790
7	.79884	.79411	.80483	1.41385	1.41618	1.42196	1.42676
8	.88409	.74349	.75348	1.42451	1.42692	1.43287	1.43784
9	.94292	.70889	.71839	1.43237	1.43487	1.44097	1.44605
	1.00000	.67573	.68472	1.44042	1.44296	1.44919	1.45444
	1.00000	.67570	.68470	1.44063	1.44316	1.44939	1.45460
	1.00000	.67570	.68474	1.44064	1.44316	1.44939	1.45462
	Mean.	.67571	.68472	1.44057	1.44309	1.44932	1.45455

TABLE IX.

Chloroform—Acetone.

No.	Δv_{25}	$\Delta v_{35.17}$	ΔRD_{25}	a_C	a_D	a_F	$a_{G'}$
1	+.00013	+.00013	+.00017	——	——	——	——
2	+ 2	− 15	+ 22	——	——	——	——
3	− 30	− 59	+ 34	5.4	5.8	5.8	5.4
4	− 75	− 111	+ 38	3.13	3.17	3.18	3.12
5	− 125	− 161	+ 28	1.89	1.94	2.04	2.02
6	− 183	− 222	+ 26	1.57	1.58	1.62	1.64
7	− 195	− 231	+ 20	1.39	1.42	1.45	1.44
8	− 157	− 178	+ 17	1.42	1.42	1.45	1.44
9	− 97	− 107	+ 9	1.29	1.36	1.38	1.36

TABLE X.

Chloroform—Acetone (Zawidzki). 35°.17 C.

x Chl.	z Chl.	$\phi_{35.17}$	$\Delta\phi$	x Chl.	z Chl.	$\phi_{35.17}$	$\Delta\phi$
0.0000	0.0000	344.5	0.0	.4934	.6672	255.5	−63.6
.0595	.1152	332.2	− 9.2	.5083	.6802	252.9	−65.5
.1217	.2218	319.9	−18.4	.5135	.6847	252.7	−65.4
.1835	.3162	307.6	−27.5	.5523	.7174	250.1	−66.0
.2630	.4234	291.0	−40.0	.5812	.7407	248.4	−66.2
.2897	.4563	285.9	−43.7	.6622	.8014	249.0	−61.5
.3613	.5379	272.9	−53.0	.8022	.8930	262.2	−41.0
.4008	.5792	267.1	−56.8	.9177	.9583	279.8	−17.6
.4240	.6023	263.1	−59.6	1.0000	1.0000	293.1	0.0

Remarks on Tables VIII., IX. and X.—A great deal of trouble was experienced in getting the results for this case. The acetone apparently absorbed moisture from the air every time the bottle was opened. The observations were repeated three times before satisfactory results were obtained. The results given are from the last set which alone are retained because they were made with acetone kept in several small bottles and also because great care was taken to thoroughly mix the liquids. These precautions seem to have entirely eliminated irregularities greater than ordinary errors of observation from the results. The error of .001 gr. in the evapo ration correction implies an error of 3×10^{-5} in z, since the amount of mixture made up in each case was never less than 30 gr. This implies an error well under the errors of observation for Δv and ΔR.

The errors in n_D are about as before, but the agreement for differences of the indices for the different wave-lengths in any given case was excellent, seldom amounting to more than 3 or 4 × 10^{-5}. The deviations for this case are plotted in Fig. 4.

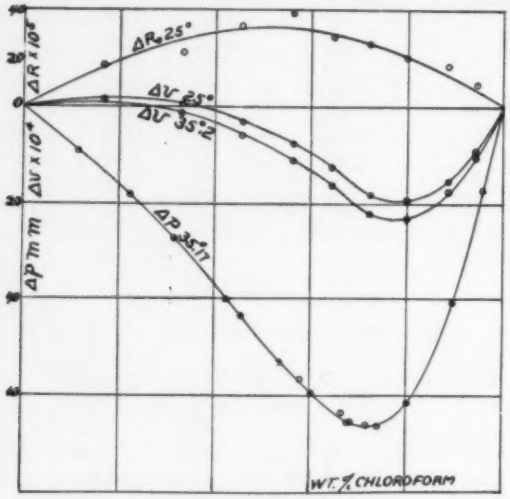

Fig. 4.

IV. *Ethyl Iodide — Ethyl Acetate.*

The ethyl iodide was washed with water to remove alcohol, dried over $CaCl_2$ with molecular silver, filtered and distilled in the usual way. It was kept in a black bottle containing a little silver — boiling point 72°.2 C. The ethyl acetate was dried with freshly ignited K_2CO_3, filtered and distilled with a micro-burner in the usual manner. Boiling point 77°.2 C. The measurements were carried out at 25° and at 50° C., the latter being sufficiently near Zadwizki's temperature (49°.99) for the pressure measurements.

Evaporation corrections: Ethyl iodide, .0075 ± .0005 gr.; ethyl acetate, .0042 ± .0005 gr.

Remarks on Tables XI., XII. and XIII. — The very great reluctance of ethyl iodide and ethyl acetate to mix is noteworthy. The smallest amount of any one mixture was 30 gr. The evaporation correction error of 5 × 10^{-4} gr. implies an error in the composition of less than 2 × 10^{-5}, which is negligible in calculating Δv and ΔR. The remarks in the preceding case concerning indices hold

TABLE XI.

Ethyl Iodide—Ethyl Acetate.

No.	x Iod.	v_{25}	v_{50}	n_C	n_D	n_F	$n_{G'}$
	.00000	1.11838	1.15874	1.36821	1.37004	1.37452	1.37822
	.00000	1.11829	1.15866	1.36822	1.37006	1.37458	———
	.00000	1.11821	1.15859	1.36822	1.37006	1.37456	1.37831
	Mean.	1.11829	1.15866	1.36822	1.37005	1.37455	1.37826
1	.19082	1.00742	1.04358	1.37943	1.38150	1.38657	1.39077
2	.35007	.91416	.94654	1.39162	1.39393	1.39964	1.40438
3	.49517	.82845	.85737	1.40563	1.40822	1.41465	1.42004
4	.59741	.76738	.79377	1.41808	1.42090	1.42800	1.43394
5	.68529	.71454	.73880	1.43092	1.43402	1.44176	1.44833
6	.74566	.67763	.70040	1.44119	1.44447	1.45274	1.45977
7	.82792	.62746	.64814	1.45757	1.46121	1.47032	1.47811
8	.89093	.58845	.60749	1.47253	1.47646	1.48639	1.49489
9	.94970	.55183	.56927	1.48898	1.49318	1.50398	1.51323
	1.00000	.52008	.53619	1.50535	1.50992	1.52159	1.53163
	1.00000	.52005	.53623	1.50534	1.50992	1.52158	1.53160
	1.00000	.52006	.53623	1.50533	1.50992	1.52158	1.53157
	Mean.	.52007	.53622	1.50534	1.50992	1.52158	1.53160

TABLE XII.

Ethyl Iodide—Ethyl Acetate.

No.	Δv_{25}	Δv_{50}	ΔR_{D25}	a_C	a_D	a_F	$a_{G'}$
1	+.00328	+.00369	−.00020	1.266	1.263	1.294	1.330
2	+ 529	+ 577	− 22	1.174	1.175	1.196	1.213
3	+ 638	+ 692	− 25	1.152	1.156	1.177	1.197
4	+ 647	+ 697	− 20	1.113	1.120	1.132	1.154
5	+ 620	+ 669	− 10	1.065	1.065	1.081	1.091
6	+ 540	+ 587	− 14	1.096	1.102	1.118	1.131
7	+ 444	+ 481	− 5	.993	1.041	1.060	1.070
8	+ 313	+ 337	− 4	1.049	1.047	1.054	1.060
9	+ 167	+ 174	− 0	.970	1.000	1.007	1.010

here also. The deviations of specific volume, refractivity and vapor pressure form their respective additive laws are shown in Fig. 5.

V. *Acetic Acid—Benzol.*

The acetic acid was Kahlbaum's best, and was further purified by fractional freezing. The benzol was boiled for three hours with

10–15 per cent anhydrous aluminum chloride under a reflux condenser. Distilled off and washed with NaOH to remove HCl, then washed with water, and, after drying over $CaCl_2$, was distilled. The fraction was collected boiling at 80°.5 C.

Evaporation corrections: Acetic acid, .0006 ± .0001 gr.; benzol, .0050 ± .0005 gr.

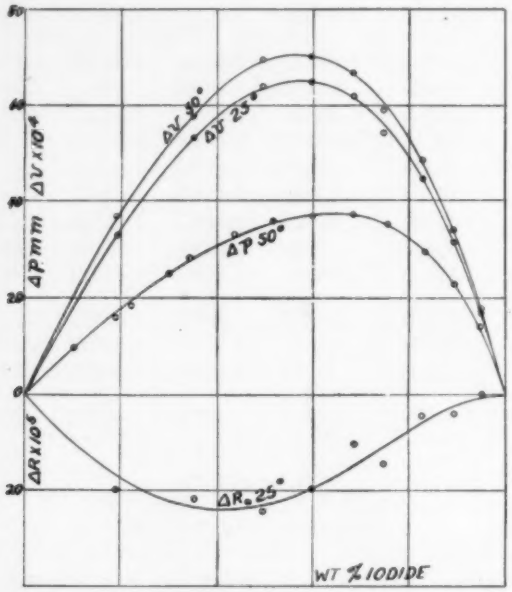

Fig. 5.

TABLE XIII.

Ethyl Iodide—Ethyl Acetate (Zawidzki). 49°.99 C.

x-Iod.	s-Iod.	$\rho_{49.99}$	$\Delta\rho$	x-Iod.		$\rho_{49.99}$	$\Delta\rho$
0.0000	0.0000	280.4	0.0	.4588	.6001	350.7	36.8
.0590	.0999	294.3	+ 9.6	.5486	.6827	357.4	37.0
.1148	.1867	304.7	15.9	.6340	.7541	361.7	35.0
.1376	.2202	308.7	18.3	.7388	.8335	363.5	29.2
.1946	.2996	319.5	24.9	.8253	.8932	363.5	22.9
.2288	.3443	325.2	28.1	.9098	.9470	360.7	13.9
.3057	.4380	335.4	32.7	1.0000	1.0000	353.4	0.0
.3745	.5158	343.4	35.7				

Remarks in Tables XIV., XV. and XVI.—The specific volumes and indices for the mixture acetic acid—benzol were easiest of all

TABLE XIV.

Acetic Acid—Benzol.

No.	s-Acetic.	v_{25}	v_{50}	n_C	n_D	n_F	$n_{G'}$
	.00000	1.14459	1.18091	1.49331	1.49794	1.50985	1.52019
	.00000	1.14458	1.18093	1.49328	1.49794	1.50985	1.52012
	Mean.	1.14458	1.18092	1.49329	1.49794	1.50985	1.52015
1	.11634	1.12768	1.16362	1.47782	1.48218	1.49323	1.50276
2	.23614	1.10923	1.14433	1.46225	1.46628	1.47644	1.48517
3	.34008	1.09194	1.12633	1.44890	1.45265	1.46208	1.47020
4	.44857	1.07299	1.10638	1.43516	1.43861	1.44724	1.45460
5	.54459	1.05549	1.08773	1.42300	1.42618	1.43414	1.44086
6	.63968	1.03692	1.06822	1.41131	1.41418	1.42150	1.42765
7	.73819	1.01687	1.04693	1.39907	1.40172	1.40827	1.41375
8	.82321	.99858	1.02776	1.38875	1.39119	1.39712	1.40206
9	.91338	.97830	1.00627	1.37803	1.38023	1.38552	1.38983
	1.00000	.95797	.98468	1.36779	1.36977	1.37440	1.37819
	1.00000	.95799	.98460	1.36774	1.36974	1.37443	1.37818
	1.00000	.95789	.98461	1.36783	1.36977	1.37444	1.37816
	Mean.	.95795	.98463	1.36779	1.36976	1.37442	1.37818

TABLE XV.

Acetic Acid—Benzol.

No.	Δv_{25}	Δv_{50}	ΔR_{D25}	a_C	a_D	a_F	$a_{G'}$
1	.00481	.00554	−.000041	1.043	1.030	1.030	1.030
2	872	976	− 12	1.010	1.005	1.011	1.014
3	1082	1217	− 82	1.032	1.028	1.029	1.019
4	1212	1351	− 115	1.037	1.036	1.041	1.042
5	1255	1370	− 157	1.048	1.049	1.050	1.053
6	1172	1286	− 184	1.051	1.063	1.058	1.054
7	1006	1091	− 229	1.088	1.093	1.100	1.102
8	764	843	− 216	1.117	1.119	1.130	1.127
9	419	464	− 118	1.114	1.121	1.126	1.195

to measure because of the low vapor pressure of acetic acid. The readings for the indices were especially sharp and constant, successive readings for a mixture agreeing within the error of the instrument, viz., 0′.5 or 5×10^{-5}, and the probable error of the measurements which are given in the tables is still smaller as they are all means of at least three; the sixth place is therefore retained for ΔR_{D25}. The relative values of the indices for a given composition

TABLE XVI.

Acetic Acid—Benzol (Zawidzki). 49°.99 C.

x-Acetic.	z-Acetic.	$\rho_{49.99}$	$\Delta\rho$	x-Ac.	z-Ac.	$\rho_{49.99}$	$\Delta\rho$
0.0000	0.0000	267.1	0.0	.3493	.4136	228.0	34.8
.0160	.0170	265.9	+2.2	.3696	.4365	224.3	35.4
.0364	.0413	265.2	5.8	.5834	.6530	189.5	45.8
.0439	.0504	264.4	6.6	.6125	.6801	184.0	46.5
.0835	.0996	261.1	11.7	.6604	.7242	175.3	48.0
.1138	.1377	259.0	16.0	.8435	.8809	126.0	37.4
.1714	.2088	250.2	19.4	.9797	.9851	68.0	8.3
.2089	.2535	245.2	22.3	.9931	.9949	59.2	2.4
.2979	.3566	236.0	32.0	1.0000	1.0000	55.4	0.0

are subject, as in the preceding case, to an error of about 2×10^{-5}, and the specific volumes are subject to a like error the error of the evaporation correction being negligible. From 30 to 60 gr. of mixture were used each time. For deviations, see Fig. 6.

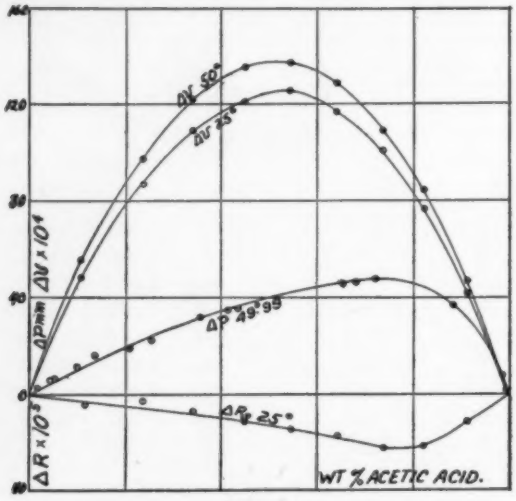

Fig. 6.

VI. *Carbon Tetrachloride—Benzol.*

The benzol used was the same as in the preceding case.

The carbon tetrachloride was dried with $CaCl_2$ and distilled. It was allowed to stand over lime to remove traces of sulphur.

Evaporation correction: CCl_4, .0090 ± .0005 gr.; C_6H_6, .0050 ± .0005 gr.

TABLE XVII.

Carbon Tetrachloride—Benzol.

No.	$x \cdot CCl_4$	v_{25}	v_{50}	n_C	n_D	n_F	$n_{G'}$
	0.00000	1.14451	1.18089	1.49332	1.49794	1.50985	1.52016
	0.00000	1.14455	1.18090	1.49327	1.49794	1.50981	1.52011
	0.00000	1.14454	1.18093	1.49330	1.49794	1.50985	1.52014
	Mean.	1.14453	1.18091	1.49330	1.49794	1.50984	1.52014
1	.16873	1.05794	1.09171	1.48973	1.49420	1.50562	1.51547
2	.31954	.98046	1.01198	1.48602	1.49030	1.50120	1.51058
3	.43419	.92179	.95150	1.48261	1.48674	1.49718	1.50613
4	.55495	.85969	.88749	1.47843	1.48232	1.49223	1.50070
5	.64704	.81251	.83881	1.47476	1.47849	1.48788	1.49592
6	.71042	.77966	.80492	1.47197	1.47555	1.48461	1.49231
7	.79671	.73562	.75943	1.46775	1.47109	1.47954	1.48668
8	.87639	.69470	.71713	1.46320	1.46629	1.47409	1.48069
9	.93504	.66449	.68589	1.45941	1.46230	1.46961	1.47576
	1.00000	.63110	.65131	1.45465	1.45733	1.46401	1.46953
	1.00000	.63109	.65133	1.45460	1.45731	1.46397	1.46952
	1.00000	.63107	.65133	1.45467	1.45733	1.46403	1.46958
	Mean.	.63109	.65132	1.45464	1.45732	1.46400	1.46954

TABLE XVIII.

Carbon Tetrachloride—Benzol.

No.	Δv_{25}	Δv_{50}	$\Delta R_{D\cdot 5}$
1	+.00004	+.00016	+.000225
2	− 1	+ 30	+ 398
3	+ 19	+ 54	+ 523
4	+ 10	+ 47	+ 497
5	+ 20	+ 56	+ 518
6	− 10	+ 23	+ 491
7	+ 16	+ 45	+ 438
8	+ 13	+ 34	+ 318
9	+ 4	+ 17	+ 179

Remarks on Tables XVII., XVIII. and XIX.—Owing to the very small values of Δv for this case the values of α have not been calculated. The magnitude of errors is in all respects as in the preceding case. For the plots of the deviations see Fig. 7.

TABLE XIX.

Carbon Tetrachloride—Benzol (Zawidzki). 49°.99 C.

$x \cdot CCl_4$	$z \cdot CCl_4$	$\rho_{49.99}$	$\Delta\rho$	$x \cdot CCl_4$	$z \cdot CCl_4$	$\rho_{49.99}$	$\Delta\rho$
0.0000	0.0000	268.0	0.0	.3953	.5630	294.5	10.7
.0507	.0952	271.8	+1.8	.5587	.7138	301.0	10.7
.1170	.2070	277.6	4.9	.6755	.8041	305.2	10.2
.1758	.2959	281.5	6.5	.7652	.8653	306.8	8.2
.2515	.3983	285.4	7.3	1.0000	1.0000	308.0	0.0
.2947	.4515	288.3	8.5				

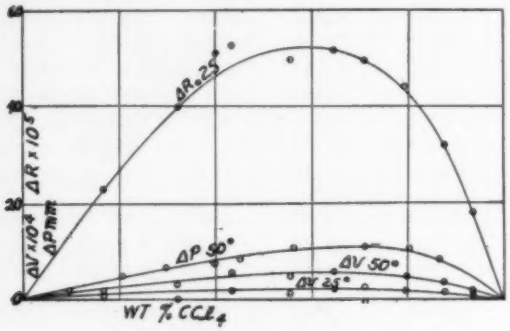

Fig. 7.

GENERAL DISCUSSION. SUMMARY.

From an inspection of the tables and figures it is seen that, for the cases studied and in the given temperature interval:

1. The deviations of the specific volumes from additivity increase in absolute value with the temperature.

A possible exception to this conclusion is found in the case of chloroform—acetone, which for a small portion of the curve seems to show a deviation diminishing with rise of temperature. This is the only mixture of the present series which shows a systematic negative deviation and the only one in which the temperature coefficient of deviation is negative. It is interesting to note in connection with this case the great heat developed on mixing which is also exceptional among the mixtures here considered. Carbon tetrachloride—benzol, according to Brown[1] shows a small negative deviation at 20° C. In the measurements here given the deviation is slightly

[1] F. D. Brown, Trans. Chem. Soc., 39, p. 202, 1881.

positive at 25° and more so at 50° C. The results for these two mixtures indicate that further study is desirable to show more completely the nature of the temperature coefficient of specific volume deviation. It seems very probable that there are mixtures in which the deviations are negative at all temperatures, others in which the deviations are always positive, other in which the deviations grow from positive to negative, still others which show the reverse, and, possibly a few which show a mixture of effects. These possibilities must be settled before binary mixtures are understood

In this connection should be noticed the interesting analogous behavior of the partial and total vapor pressures; *i. e.*, that their deviations from additivity also increase in absolute value with the temperature. This was brought to my attention by Professor Rosanoff who has kindly furnished the following proof. Let P_1 and P_2 be the respective vapor pressures of the pure liquids A and B, and let p_1 and p_2 be the respective partial vapor pressures of A and B in the mixture A-B. Also let p_1' and p_2' be the respective partial pressures calculated on the assumption of simple additivity, thus, $p_1' = P_1x$ and $p_2' = P_2(1 - x)$. We have

$$p_1 = P_1 f(x),$$

hence

$$p_1 - p_1' = P_1\{f(x) - x\} = P_1\varphi(x).$$

Rosanoff and Easley (*loc. cit.*) have shown that $f(x)$ and, accordingly, $\varphi(x)$, in those cases in which the heat of dilution is moderate, is practically independent of the temperature. Hence, where this is true, for any given value of x, the deviation of the partial vapor pressure p_1 from additivity is

$$\Delta p_1 = p_1 - p_1' = kP_1,$$

where k is constant. Since P_1 increases with the temperature, therefore must Δp_1 increase in absolute value with the temperature. Similarly for $\Delta p_2 = p_2 - p_2'$; and hence, also, *the deviation of total vapor pressure, $\Delta p = \Delta p_1 + \Delta p_2$ must increase in absolute value with the temperature.* The analogous behavior of specific volume deviations in these mixtures is striking and suggestive.

2. The algebraic sign of the deviation of specific volume is the same as that of the vapor pressure at the same temperature.

This conclusion, together with (1), suggests the possibility of the vapor pressure deviation changing sign as the temperature is varied, and also, judging from the vapor pressure and volume curves of chloroform—acetone, that there may exist curves of the mixed type, part positive and part negative. These curves have already been predicted but have not as yet been found.[1] It is possible that chloroform—acetone may yield such a curve at a low temperature.

3. The deviations of refractivity are of the same sign as the deviation of vapor pressure and specific volume in the cases of CS_2—methylal, CS_2—acetone and CCl_4—C_6H_6, and of opposite sign in the others. The deviations show an increase in absolute value with diminishing wave-length. The Pulfrich constant α is seen, in some cases to vary within wide limits. The Pulfrich equation is empirical and the constant α has no theoretical significance. The expression for the refractivity has not as yet taken a final form (see above), and until we know more about the dispersion of pure liquids it would seem to be very difficult to correlate deviations of refractivity ΔR with the deviations of density and vapor pressure. The values of ΔR are accordingly given here for but one wave-length, that of sodium. On account of the excellent uniformity shown by the differences of the indices for different wave-lengths the indices for all the wave-lengths are given in the hope that they may be useful for further calculation. Greater knowledge of the dispersion of binary mixtures may be expected from a study of their absorpton bands in the ultra-violet and in the infra-red.

It is the intention of the author to add results for other mixtures, making available for further study the binary systems *A-B*, *B-C*, *A-C*, to settle the question whether the deviations are additive from mixture to mixture or whether they depend upon the specific action of two given liquids upon each other.

The present results have been considered from the standpoint of Dolezalek's theory (*loc. cit.*), which attempts to explain all deviations by assuming dissociation of polymerized molecules, or combination of the two components, *i. e.*, putting the matter upon a

[1] See Zawidzki, Zs. für phys. Chem., LXIX., p. 630, 1909.

chemical basis. The results of these calculations will be published in a subsequent paper.

The measurements presented in this paper were made in the summer and fall of 1908.

CLARK COLLEGE, WORCESTER, MASS.,
March, 1910.

ON ENTROPY.

BY W. S. FRANKLIN.

IT has perhaps occurred to every student of thermodynamics that there might be a simple and direct method of establishing the quantitative idea of entropy, considering that the idea is so widely applicable and that it is independent of the properties of particular substances and independent of particular processes. The difficulty is that the definite forward movement in nature which has been formulated as the law of increase of entropy is mixed up inextricably with changes of state of physical substances. This difficulty is met in the argument of Clausius by considering a cyclic process where no change of state is left outstanding, but it is apparently an unnecessary complication to base the discussion of a definitely forward moving quantity like entropy upon a cyclic process. Clausius's integral, moreover, is strictly applicable to reversible processes only, and in Clausius's argument, when limited in this way, the law of increase of entropy makes its appearance as follows: Consider a state B which is reached from state A by an irreversible process, then Clausius's integral extended over a reversible process leading from state A to state B gives a positive result. For example, a gas issues from an orifice in a high pressure tank, and if the gas is brought from its initial condition to its final condition by a reversible process, Clausius's integral extended over this reversible process gives the increment of entropy which is associated with the original irreversible process. To base the discussion of the law of increase of entropy upon reversible processes only (and this is substantially what Clausius's original argument does, considering that the application of Clausius's integral to irreversible processes is not legitimate) would seem to be to ignore a most important physical element, because the quantitative idea of entropy gains its significance chiefly in its application to irreversible processes.

The object of this paper is to call attention to a class of irrever-

sible processes which are permanent or steady and therefore susceptible to quantitative treatment, and which lead to no change of state of any kind so that the entropy changes which are involved are associated solely with energy transformations. By a careful consideration of an irreversible process of this type the quantitative idea of entropy may be established in the most direct possible way. The quantitative idea of entropy when established in this way is quite primitive and highly generalized and it refers to the entropy increment involved in the conversion of work into heat or to the entropy increment involved in the flow of heat from a high-temperature region to a low-temperature region, and a further development of the idea of entropy is of course necessary in order to establish a measure of the entropy differences which are associated with changes of state. This extension of the primitive idea of entropy can be established only by a consideration of a cyclic process.

A further object of the paper is to discuss an apparent close relationship between entropy and time.

The simplest kind of irreversible process is that which takes place in an isolated system while the system is settling to thermal equilibrium. Such a process has a certain impetuous quality as, for example, in a conflagration, when a house is settling to thermal equilibrium with the surrounding air, and perhaps the physical nature of an irreversible process is most clearly and strongly suggested by speaking of such a process as a *sweeping process* or as a *sweep*. A careful consideration of the various sweeping processes which take place in nature leads to the recognition of three distinct types as follows: (*a*) Sweeping processes which take place in a closed system, (*b*) sweeping processes which take place in a system which is subjected to rapidly varying external action, and (*c*) sweeping processes which are perfectly steady and which involve no changes of state of any kind in the system under consideration. The first type is exemplified by the explosion of a mixture of hydrogen and oxygen in a closed vessel. The second type is exemplified in the departure from thermal equilibrium of a gas which is rapidly compressed under a piston or by the departure from thermal equilibrium of a vessel of water which is heated on a stove. In both cases the system never catches up, as it were, with the changing conditions but trails along

behind them. The third type is exemplified by the flow of electric current through a wire from which heat is abstracted by a steady stream of air or water, and by the steady flow of heat from a region of high temperature to a region of low temperature. A number of years ago I suggested the terms "simple sweep," "trailing sweep" and "steady sweep," respectively, to designate these three types of irreversible processes. The entropy change which accompanies a simple sweep is involved in or associated with the change of state of the substance. The entropy change which accompanies a trailing sweep is associated in part with the conversion of work into heat, in part with the flow of heat from a region of high temperature to a region of low temperature, and in part with the changes of state of the substance. The entropy change which takes place in a steady sweep is due solely to the conversion of work into heat or to the transfer of heat from a region of high temperature to a region of low temperature, or both. Therefore a careful consideration of a steady sweep is the simplest basis for the discussion of the idea of entropy.

In establishing the idea of entropy it seems to be necessary to start out with the assumption that the entropy function exists, and then to justify this assumption by logical deductions and experimental verifications. Clausius, indeed, starts with the assumption that a non-compensated transfer of heat from a cold region to a hot region is impossible. This form of assumption may seem to obviate initial reference to the entropy function but it is not accompanied by a clear and complete definition of compensation in the thermodynamic sense, and indeed such a definition cannot be stated without the introduction of the idea of entropy. It is evident, therefore, that the idea of the entropy function is really involved at the very beginning of Clausius's classical argument, and a logical development of the second law of thermodynamics might perhaps be made less indefinite and more intelligible by frankly introducing the idea of entropy at the start in explicit terms. Indeed this is the procedure which is adopted by Professor Planck. It is difficult, however, to give a preliminary definition of entropy which is correct as far as it goes and which carries an appeal to one's primitive sense of physical things. Such an appeal is greatly to be

desired and it is certainly possible because there is perhaps a more widespread intuitive sense touching the second law of thermodynamics than in the case of any other of the generalizations of physics.

Fire is the most familiar example of a sweeping process and its most striking characteristic is that its progress is not dependent upon any external driving cause; when once started it goes forward of itself and with a rush. Everyone perhaps will admit that the impetuous character of fire suggests a certain havoc, a certain degeneration or waste in the system in which the fire takes place, and the same is true of every sweeping process. Consider, for example, a charge of gunpowder which has been exploded in a large empty vessel; everything is there after the explosion, all of the energy is there and all of the material substance is there, and yet it cannot be exploded a second time! But the man on the street has heard so much during recent years of the conservation of energy and of the conservation of mass that the old proverb that "You can't eat your cake and have it" presents to his mind a very simple and inevitable fact or condition which he is at times tempted to ignore when he turns his attention to an unfamiliar matter like the steam engine; he tries in vain to rationalize steam engine theory in terms of the principles of conservation alone. Nearly all of the intuitive sense of the man on the street concerning such matters (and he has a great deal) is involved in the second law of thermodynamics which is not a law of conservation at all; it is a law of waste.

It may be assumed that every sweeping process brings about a definite amount of degeneration, an amount that can be expressed numerically. Thus a certain amount of degeneration may be assumed to be brought about when a compressed gas escapes through an orifice, when heat flows from a region of high temperature to a region of low temperature, when work is converted into heat by friction or by the flow of an electric current through a wire, and so on. In a simple sweep the degeneration lies wholly in the relation between the initial and final states of the substance. In a trailing sweep the degeneration may lie partly in the relation between the initial and final states of the substance which undergoes the sweep,

partly in the conversion of work into heat, and partly in the flow of heat from a high temperature region to a low temperature region. In a steady sweep, however, the degeneration lies wholly in the conversion of work into heat, in the transfer of heat from a region of high temperature to a region of low temperature, or in both. Therefore the idea of thermodynamic degeneration as a measurable quantity can be reached in the simplest possible manner by a careful scrutiny of a steady sweep.

Proposition (*a*).—The thermodynamic degeneration which is represented by the direct conversion of work into heat at a given temperature is proportional to the quantity of work so converted. Consider, for example, a steady flow of electric current through a wire from which the heat is abstracted continuously so that the temperature of the wire remains constant. This is a steady process, that is to say, it remains unchanged during successive intervals of time, and therefore any result of the process must be proportional to the time. Thus the amount of degeneration occurring in a given interval of time is proportional to the time, but the amount of work which is degenerated into heat is also proportional to the time. Therefore the amount of degeneration is proportional to the amount of work which is converted into work at the given temperature.

Proposition (*b*).—The thermodynamic degeneration which is represented by the transfer of heat from a given high temperature T_1 to a given low temperature T_2 is proportional to the quantity of heat transferred. Consider a steady flow of heat from temperature T_1 to temperature T_2 constituting a steady sweep, a sweep which remains unchanged in character in successive intervals of time. Any result of this sweep must be proportional to the time and therefore the degeneration which takes place in a given interval of time is proportional to the time; but the quantity of heat transferred is also proportional to the time. Therefore the amount of degeneration is proportional to the quantity of heat transferred from temperature T_1 to temperature T_2.

According to proposition (*a*), above, the thermodynamic degeneration which is involved in the conversion of work into heat at a given temperature is proportional to the amount of work so converted and the proportionality factor depends upon the temperature only. Therefore we may write

$$\varphi' = m_1 W, \tag{1}$$

$$\varphi'' = m_2 W, \tag{2}$$

in which φ' is the degeneration involved in the conversion of an amount of work W into heat at temperature T_1, and φ'' is the degeneration involved in the conversion of an amount of work W into heat at temperature T_2, and m_1 and m_2 are factors which depend only upon T_1 and T_2, respectively. An amount of work W having been converted into heat at temperature T_1, imagine the heat to flow to a lower temperature T_2, thus involving an additional amount of degeneration according to proposition (*b*) above. The conversion of work W into heat at temperature T_1 and the subsequent flow of this heat to a lower temperature T_2 gives the same result as would be produced by the conversion of the work into heat at the lower temperature directly. Therefore the lower the temperature at which work is converted into heat the greater the amount of degeneration involved. That is to say, the factor m_2 in equation (2) is larger in value than the factor m_1 in equation (1), temperature T_1 being higher[1] than temperature T_2. Therefore, since m_1 and m_2 depend only upon T_1 and T_2, respectively, it is permissible to adopt the equation

$$T_1/T_2 = m_2/m_1, \tag{3}$$

as the definition of the ratio T_1/T_2.

Another way to express the definition which is involved in equation (3) is as follows: Considering that the factor m_1 is the smaller the higher the temperature T_1, we may adopt k/m_1 as the measure of the temperature T_1, and k/m_2 as the measure of the temperature T_2, giving

$$m_1 = k/T_1, \tag{4}$$

$$m_2 = k/T_2, \tag{5}$$

where k is an indeterminate constant. Therefore equations (1) and (2) may be written in the general form

$$\varphi = kW/T, \tag{6}$$

[1] The idea of higher and lower temperature is not dependent upon any method of measuring temperature.

where φ is the thermodynamic degeneration involved in the conversion of an amount of work W into heat at temperature T, and k is an indeterminate constant.

Since the factor k in equation (6) is indeterminate, we may adopt as the unit of thermodynamic degeneration the amount which is involved in the conversion of one unit of work into heat as a temperature of one degree on the absolute scale; then the value of k is unity and equation (6) becomes

$$\varphi = W/T, \tag{7}$$

in which W is expressed in joules, T in degrees centigrade and φ in joules per degree. Thus one joule per degree is the degeneration involved in the conversion of one joule of work into heat at 1° C. on the absolute scale.

To convert an amount of work W into heat at temperature T_1 involves W/T_1 units of degeneration. To convert the same amount of work into heat at temperature T_2 involves W/T_2 units of degeneration. Therefore to transfer an amount of heat equal to W from temperature T_1 to temperature T_2 must involve an amount of degeneration equal to the excess of W/T_1 over W/T_1, or an amount equal to $W(1/T_2 - 1/T_1)$, or $H(1/T_2 - 1/T_1)$, where H is the amount of heat transferred.

The word degeneration as used in the above discussion means the same thing as entropy increment, and the word degeneration is used because it carries with it a suggestion of irreparable waste. Furthermore, it is desirable to reserve the word entropy until with the help of Clausius's integral we are able to assign a definite entropy-difference to a given difference of state of a substance so that, choosing a zero state of the substance arbitrarily, we may speak of the entropy-of-the-substance in any other given state.

Starting with the above ideas of thermodynamic degeneration and remembering that such degeneration occurs only in sweeping processes, it is easy to establish the important proposition that the efficiency of a reversible engine depends only upon the boiler and condenser temperatures, and it is easy also to transform the

above definition of temperature ratio as given in equation (3) to the form in which it was originally given by Lord Kelvin.[1]

The Relationship of Entropy and Time.

The above propositions concerning the entropy increment which is associated with a steady sweep suggest a relationship between entropy and time, and it is desirable to carry the inquiry further to determine whether this relationship is a fundamental one or not. It seems, indeed, at first sight, as though there could be no fundamental relationship between entropy and time because entropy increases with the utmost irregularity in different parts of the universe whereas time is thought of as a universal steady flux.

Imagine an isolated mechanical system involving no irreversible processes. After a sufficient length of time, using that term in the commonly accepted sense, the system returns to identically its initial state, and when the system has returned to its initial state it is unjustifiable to project into the system the idea that there has been a lapse of time. It seems, of course, absurd to make this statement because everyone realizes in looking at the ideal mechanical system that time has elapsed between its initial and final state, but this view of the matter involves the inclusion in our ideal system of one's own physical body and the projection of one's own consciousness into the aggregate of phenomena under consideration. Let us, therefore, consider our ideal system apart from its relation to any outside condition whatever. Then, to say that time has elapsed when the system has returned to its initial state is to introduce an arbitrary and meaningless difference between the initial and final state.

Consider a system in which no changes whatever are taking place. What we call the lapse of time finds no basis for its application to such a system because no progressive change of any kind is taking place in the system.

Consider a purely mechanical system (one in which no irreversible action takes place). Any change in state of this system after the lapse of what we call time can be completely specified in terms of

[1] These arguments are outlined in a very simple way in an article by W. S. Franklin in Popular Science Monthly, March, 1910.

the positions and velocities of the component parts of the system, and it must be remembered that in specifying the velocities of the component parts of the system no reference need be made to the time which has elapsed since the beginning. That is to say the complete specification of the change of state of the system may be made without reference to the lapse of time, and to say that time has elapsed is to introduce an arbitrary and meaningless difference between the initial and final states of the system in addition to the differences already completely specified in mechanical terms.

Consider a system in which irreversible processes take place. Such a system departs further and further from its initial condition without possibility of return and in this case a complete specification of change in the system can be made in terms of mechanical specifications and entropy specifications, and it would seem to be meaningless to add the further specification of lapse of time to what is otherwise complete.

What we call time, when reduced to its simplest terms, is a phenomenon of consciousness. And our sense of the inevitable forward movement of time is dependent upon the existence of irreversible processes everywhere about us, and especially inside of us. That is to say, our sense of the forward movement of time and the law of increase of entropy are based upon or grow out of the same fundamental conditions in nature.

The above argument would seem to indicate that the universal steady flux of time is an idea, and not a physical fact; although, taking the universe as a whole, local irregularities become individually negligible and the entire process of nature may be thought of as one vast steady sweep in which increase-of-entropy and passage-of-time, much as they differ in our local methods of measuring them, refer fundamentally to the same thing. The extent to which the idea of the steady flux of time pervades our habitual modes of thought seems to be an outgrowth of the methods that we have come to use in the expression of our rather complicated experiences relating to what we call coincidences in time. Indeed some of the most pervasive things of the human mind are the ideations which have been developed as bases for our system of language, and to make due allowance for them in a physical discussion is sometimes

very difficult indeed, partly because we fail to recognize the ideations as such and partly because we are left without any adequate forms of expression if we set them aside. We always make time specifications with respect to a recurrent phenomenon like the rising of the sun, with finer gradations based upon the oscillations of a pendulum; our time specifications are simple counts of these recurrent phenomena; and the requirement of simplicity and directness of speech has led to the development of the idea of the steady flux of time and to the habitual projection of this idea into every objective condition we encounter in nature.

Two phases of two systems are simultaneous or coincident in time when they involve the loss of energy by one of the systems and the gain of energy by the other system. Thus it seems that the idea of simultaneity rests fundamentally upon the principle of the conservation of energy. If energy could be taken from one system, temporarily annihilated, and later delivered to another system, our idea of simultaneity would have to be modified; or if energy is taken from one system and if some time must elapse before its delivery to another system, as in the case of the transmission of energy by a beam of light, then again a modified conception of simultaneity would have to be developed. Indeed, this modified idea of simultaneity is already accomplished in terms of the idea that light has a definite velocity, and it seems as if the modern principle of relativity may lead to another solution of the same problem. The idea that it is everywhere *now* cannot be justified in the physical nature of things although an assumption to that effect is extremely convenient in speech. Also the idea that time is a universal steady flux cannot be justified in the physical nature of things although an assumption to that effect is extremely convenient in speech. Indeed, throughout the above discussion modes of expression are used which involve the common idea of time as a steady flux and to avoid the use of these common modes of expression would make the discussion extremely difficult to follow.

LEHIGH UNIVERSITY,
February 22, 1910.

THE EFFECT OF PRESSURE ON THE ALUMINUM RECTIFIER.[1]

BY A. P. CARMAN AND G. J. BALZER.

THE peculiar action of the electrolytic cell with aluminum anode has been the subject of much investigation since it was first observed by Buff in 1857,[2] but the interest has been heightened within recent years, because of the increasing demand for a rectifier for alternating currents, and because the newer theories of solution and of electrons have suggested new explanations of the cell. Within a half dozen years, the important part played by the gas formed on the anode has been urged by several writers on the action of the cell.[3]

It suggested itself to the writers of the present paper, that light would be thrown on the problem by determining the exact effect of pressure on the action of the cell when traversed by an alternating current. For this purpose small cells were made, and placed under a cast-iron bell jar, so that the pressure could be raised from nearly zero to several atmospheres. The wave forms of the alternating current were photographed with an oscillograph, and at the same time, readings were made of the current and the electromotive force with Weston ammeter and voltmeter. All the cells had aluminum anodes and carbon cathodes. Fig. 1 gives all the description needed of the mechanical features of the cell. The evaporating dishes used were 10.5 cm. in diameter, and as indicated in the figure, were placed inside of larger dishes for packing the cell in ice. In most of the experiments, the temperature of the cell was kept about 2° C. The resistance of the cell was varied by varying the size of the anode; in some cells an aluminum wire of about 1 mm. diameter

[1] Paper read before the American Physical Society, Boston, December, 1909.

[2] Buff, Liebig's Ann., 1857, p. 296.

[3] Guthe, PHYS. REV., Vol. XV., p. 327, 1903. Schulze, Ann. d. Physik, 21, p. 955; 22, p. 543; 26, p. 372; 28, p. 787.

was used, and in others a vertical plate. Electrolytes used in the experiments were solutions of alum, of sodium borate, of bichromate of potassium and of potassium phosphate. When such a cell is placed in an alternating current circuit, the current becomes apparently unidirectional. The oscillograph curves show that the resulting current is practically a series of unidirectional pulses. That is, provided the impressed E.M.F. is not above a certain critical value, the current wave in one direction is practically cut out, the current passing freely from carbon to aluminum, but not from aluminum to carbon. To get this rectifying action quickly we employed the usual device of first forming the cell with a direct

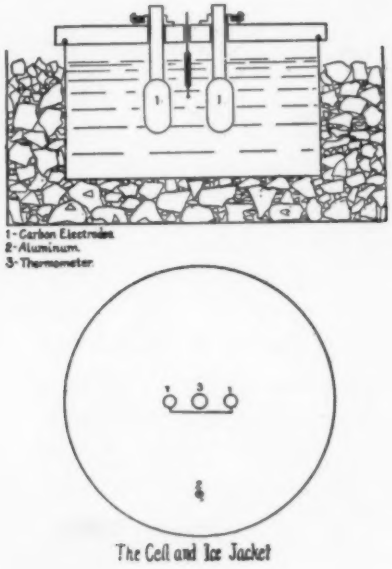

Fig. 1.

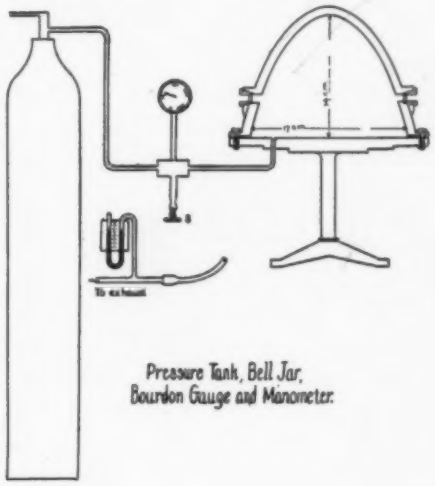

Fig. 2.

current. The alternating current was taken from the lighting and power circuits of the university system. The loads on the line were frequently changing, and so the wave forms changed. This hampered the work, and our curves often had to be taken late at night when the load on the lines was constant. In future work, a motor generator set, driven by a current from a storage battery, is to be used, but this was not available for the present experiments.

To vary the pressure, the cell was placed under a cast-iron bell jar, the arrangement being shown in Fig. 2. Small windows of heavy glass were placed so that the cell would be watched, and the temperatures read. To obtain uniform pressure, compressed air was taken from a cast-iron cylinder which had been charged to a pressure of about 1,000 lbs. per sq. in. from the compressor of the liquid air plant. The Duddell oscillograph was fitted with a home-made vertical slide, and the photographs were taken on 4×5 inch glass plates, the amplitude of the waves on the plate being generally about 4 cm. Fig. 4 shows the effect on the alternating current of the increase of pressure on a cell with a solution of sodium borate, the temperature being kept constant at 2.1° C. The pressures here increase successively from 8 mm. of mercury to 21 atmospheres. Fig. 5 shows the successive curves for the same cell as the pressure increases. These curves show that the rectifying action decreases with increasing pressure, and that the cell practically recovers its action when the pressure is removed. Similar curves were taken for cells with other electrolytes, showing that pressure decreased the rectifying action, though not always as much as in this case. In Fig. 6 we have curves for increasing pressures with a potassium bichromate cell, and in Fig. 7 we have similar curves for an alum cell. Readings of the current and of the electromotive forces were also made, in most cases, the instruments being kept in only during the times of reading. The readings of the voltmeter placed across the cell show only relative values, because the resistance of the low reading Weston voltmeter was not large compared with the resistance of the cell. A low reading electrostatic voltmeter was not available. Table I. shows the course of these readings for the alum cell with increasing and decreasing pressures.

These readings show the apparent decrease of resistance with increasing pressure, but the oscillograph curves are needed in any interpretation of the readings.

The experiments described above were all made at practically the same temperature, about 2° C. It suggested itself to us to try the effect of changes of temperature. Fig. 8 gives a series of oscillograph curves made for an alum cell, with temperatures increasing from 2.1° C. to 50° C. It is seen that the increase of temperature

Fig. 3.

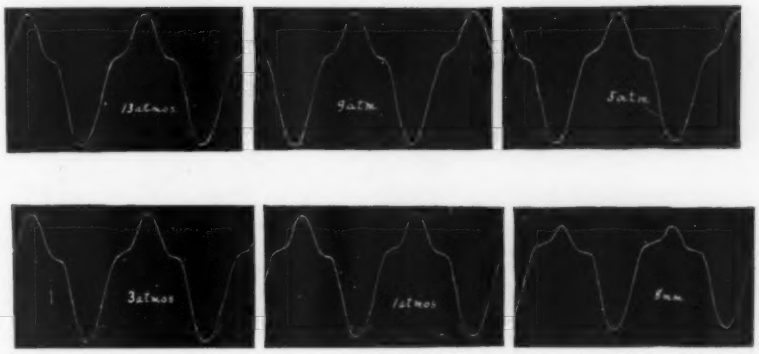

Fig. 4.

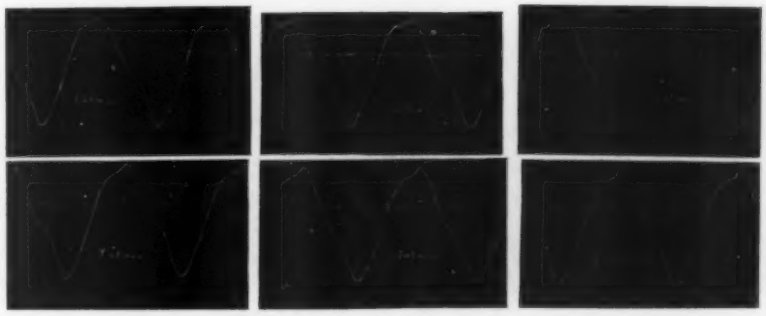

Fig. 5.

CARMAN AND BALZER

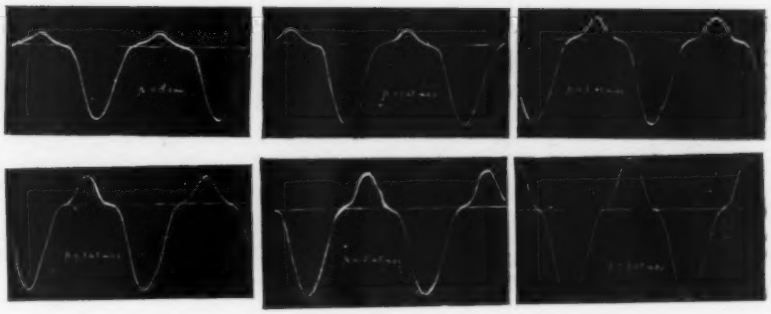

Fig. 6.

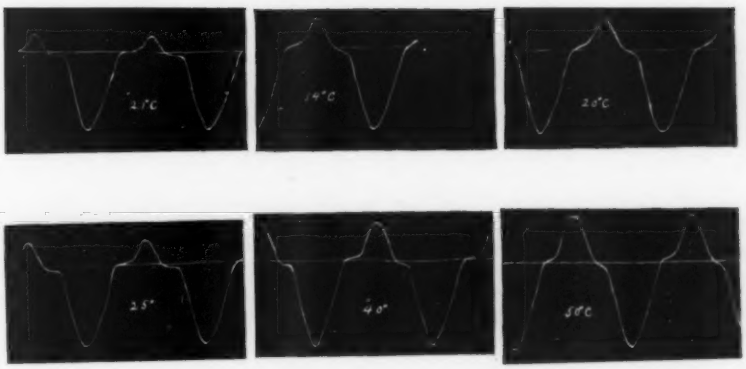

Fig. 7.

TABLE I.

Cell with Aluminum Anode and with Alum Solution.

Pressure.	E.M.F. Across Cell.	E.M.F. Impressed.	Current (Amp.).
.8 cm.	24.5	32.2	.21
1 atmosph.	23.5	32.3	.22
2	22.1	32.2	.24
3	21.5	32.1	.25
5	19.7	32.2	.26
7	19.0	32.3	.27
9	18.5	32.4	.28
11	17.8	32.5	.29
13	17.4	32.3	.29
15	17.0	32.2	.29
17	16.5	32.3	.30
21	16.3	32.2	.31
17	16.4	32.3	.33
15	16.8	32.3	.33
13	16.9	32.2	.33
11	17.0	32.2	.32
9	17.0	32.1	.32
7	17.5	32.2	.30
5	18.2	32.2	.29
3	18.6	32.2	.28
2	19.3	32.3	.27
1	20.5		.26
.8 cm.	25.6		.17

decreases the rectifying action for this particular solution. The cell did not recover the rectifying action when the temperature was lowered again—a fact which has perplexed us. Of course the temperature fall was slow, and during this fall it was difficult to keep other conditions perfectly steady, but there was certainly a permanent change following the rise in temperature. This temperature effect probably depends also upon the temperature at which the cell is originally formed.

Numbers of investigators of the action of the aluminum cell have studied the character of the solid oxide film which is formed on the aluminum anode. The differences in the explanations of the cell are largely differences in the part ascribed to this solid film. Some writers have thought that the cell's action depended upon active selective properties of the film, while Schulze, who has pub-

lished five or six investigations on this within the last few years, makes the action of the film wholly or almost wholly mechanical. According to him, it supports the gas film, which forms between the solid oxide deposit and the aluminum plate.

He says:[1] "The electrolytic valve action is not due to the rigid layer, which forms on the valve metals, but to a much thinner gas film which exists in the pores of the rigid layer and separates the electrolyte from the metal. If the valve metal is the kathode, then the free electrons contained in it pass through this gas layer with a comparatively small fall of potential. If the valve metal is the anode, a high difference of potential is necessary because there are then no free electrons in the electrolyte. I conclude, that the negative electrolytic ions then take the place of the electrons, and the ions, on account of their greater mass, experience a much higher resistance in the gas layer than that which the free electrons encounter in the opposite direction. This explains the so-called valve action."

The effect of pressure on the rectifying action, or "valve action" (Ventilwirkung), as Schulze calls it, is readily explained in accordance with Schulze's conceptions. The gas layer is reduced in thickness by the pressure and hence the resistance of the layer is decreased. We also observed a phenomenon which puzzled us at the time, but which is readily explained on the supposition of gas layers imprisoned in the body of the rigid film or behind it. The phenomenon was that at higher pressures a white fluffy deposit resembling in appearance the white of a boiled egg began to form at the aluminum anode and this increased as the pressure increased. This fluffy deposit would sometimes leave the electrode and rise to the top, or sink to the bottom. As the pressure was released the deposit decreased, and at low pressure dropped to the bottom almost entirely. Evidently the solid film was broken by the pressure of the gas, and the fluffy deposit was the disintegrated film.

The effect due to rising temperature which we observe is not explained so evidently. It would seem that the solid oxide film was rendered more porous by the temperature increase, and hence

[1] Schulze, Ann. d. Physik, 28, p. 787.

the gas layers were dissipated, that is, the formation on the plate was destroyed. This would accordingly not recover immediately. The temperature effects however require more investigation.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
December, 1909.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

THE RELATION BETWEEN ZERO SHIFT AND SIZE OF WIRE IN THE MOVING COIL GALVANOMETER.[1]

BY WALTER P. WHITE.

THE displacement of zero usually produced by the deflection of a moving coil galvanometer is at present one of the most serious sources of inconvenience or error with that instrument and is not so well understood as most other features of the design. It increases, of course, with the magnetic impurity of the materials in the coil, and is diminished by the use of a radial field. For both of these further study seems desirable. It also depends on the coil constants, and in the following way: Let F be the proportion of "dead" material (frame, horizontal wire, mirror, etc.) in the coil, let X be the proportion of magnetic impurity in the coil material lying in the field, K the moment of inertia of the coil, T the periodic time, R the critical or total circuit resistance, V the voltage sensitiveness, d the diameter of the wire in the coil. The torque due to magnetic impurity will be taken as proportional to the square of the field strength and to the total amount of magnetic impurity lying in the field — which is true to a very close approximation. Then, from equations previously given[2] it is easy to show that the zero displacement for a given deflection is proportional to

$$\frac{X}{1-F}\frac{RT}{K}d^4, \quad \text{or to} \quad \frac{X}{1-F}\frac{V^2R^2}{T^2}d^4.$$

That is, for a coil of given performance, zero shift increases with the size of wire used and with the dead material, and when so expressed is independent of the field strength, shape of coil, etc., except as the shape

[1] Abstract of a paper presented at the Washington Meeting of the Physical Society, April 22–3, 1910.

[2] Everyday Problems of the Moving Coil Galvanometer, Walter P. White, PHYS. REV., XXIII., 382, 1906.

affects the amount of dead material. It increases with the excellence of the galvanometer as measured by the smallness of K, that is, by the delicacy of the coil; for a given coil it is less for shorter periods. If, however, the shorter period is added to a given sensitiveness, which involves a further increase in the galvanometer performance, the shift increases. If the shift is diminished by diminishing the size of wire in the coil, this may increase the coil resistance. Hence an *unnecessarily* small coil resistance may prove a detriment in moving coil galvanometers. If finer wire is used, the resistance and moment of inertia of the coil can be kept constant by increasing the width. This change will require a stronger field, hence in such a case the use of a stronger magnet actually contributes toward reducing the error from magnetic impurity in the coil. Of course, a decrease in the size of wire increases the relative weight of the insulation, and therefore increases the constant, F. An exact estimate of this effect is impossible, as long as the constants of the particular wire and the distribution of the magnetic impurity between metal and insulation are unknown, but a rough calculation indicated in one case (for silk insulation) that the magnetic difficulty is not likely to be diminished by reducing the diameter of the wire below 2 mils (.05 mm.).

For ballistic galvanometers, a long period is desired, and it is clear from the first expression above that as far as zero shift is concerned the increase can best be obtained by increasing K, the moment of inertia of the coil. In that case, since T only increases as the square root of K, the zero shift will actually diminish. The ballistic sensitiveness, however, is proportional to the square root of T/K, hence this change reduces the sensitiveness and may sometimes be undesirable. Since, however, the second expression above becomes, for the ballistic galvanometer,

$$\frac{X}{1-F} V^2 R^2 d^4$$

the increase of period will not increase the zero shift unless the sensitiveness is actually increased at the same time. As to the factor F, the practice of weighting the coil increases it and hence is undesirable as far as magnetic difficulties are concerned. It is better to increase either the number of turns of wire, or, if this would give too high resistance, the width of the coil. Of course, an extreme increase in coil width also increases the factor F unduly. The best arrangement in any given case may depend upon the balance of advantage among a number of different factors, which is too complicated for formulation.

NEUTRAL CONTACTS AND SWITCHES.

BY WALTER P. WHITE.

THE potentiometer is a more recent instrument than the wheatstone's bridge. In many cases, apparatus and methods for electrical measurements are now adapted to resistance measurements, where low-resistance contacts are imperative and thermal electromotive forces must take care of themselves. With the newer methods of measuring electrical quantities by means of electromotive force rather than by resistance, this necessity for small contact resistance largely disappears, and it becomes possible to gain a decided advantage by using neutral contacts, that is, contacts which are free from electromotive force. Such a contact is also needed at one point in a potentiometer system.

One requirement for a neutral contact is of course obvious, namely, that both metals be alike thermoelectrically. Another less familiar requirement is that there shall be no temperature gradient across the contact surface, since in that case the surface layer of the metal, always different from the inside, will form with it a thermoelement. The necessary elimination of temperature gradient is most easily secured by making the contact between two thin strips of metal (from .1 to .3 mm. thick), one of them backed by cork or other thermal insulator. The easiest way to get homogeneous metal is also to cut strips from the same sheet, hence practically the essential of a neutral contact is the use of two thin strips of the same sample of metal. When one side of such a combination was placed in direct contact with a plate heated 45° above room temperature, the resulting electromotive force in the contact was too slight to measure, that is, less than .1 microvolt. Under ordinary temperature conditions, therefore, such contacts are practically quite neutral. The metal need not be copper, but if it is not, junctions where the switch metal joins copper must enter as pairs oppositely directed in the circuit, and these must be small, close together, and well shielded, so that the temperatures of the two junctions shall always be the same.

Three forms of neutral contact have been found useful: (1) A sliding contact, much like an ordinary switch, can be arranged with thin strips of metal. (2) Two tongues of metal can be pressed together directly without sliding. Even with copper such an arrangement requires surprisingly little cleaning, and it produces a switch of very simple construction. One rather complicated switchboard was constructed in this way without a single soldered joint. The resistance of such a contact with about 1 kg. pressure is about the same as that of the best sliding

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 22–3, 1910.

switches. (3) A tongue of copper pulled through an ordinary wooden clothespin can be clamped upon a similar strip, forming a remarkably cheap and very effective neutral contact for semi-permanent connections, or even, in some cases, for use as a switch contact.

The last form of contact has decided advantages aside from its neutrality. Compared with a binding post, it is quicker to manipulate and yet much less likely to become loose, is much more adaptable and convenient, and is inferior only in its slightly greater bulk. A cable with such contacts at its ends, ready for instant connection to almost anything, is a very convenient laboratory appliance. By the aid of a couple of strips of celluloid, equally convenient two-pole contacts of this type can also be made.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C.,
May 5, 1910.

A SPECIAL FORM OF SURFACE BOLOMETER FOR TOTAL RADIATION EXPERIMENTS.

BY E. F. NORTHRUP.

THE apparatus consists, essentially, of two flat spirals of very fine insulated wire which form two arms of a wheatstone bridge. The flat spirals used are each 4½ cm. in diameter. They are wound with 2 mil silk insulated nickle wire and cemented to very thin sheets of mica. These flat disk spirals are mounted with their faces opposed in a box which replaces a Lummer-Brodhun screen on a photometer bench. When equal radiation from two incandescent lamps falls on the two disks, the wheatstone bridge is balanced. If one lamp gives more total radiation than the other the balance of the bridge is restored by moving the bolometer along the photometer bench to obtain the balance in precisely the same way as a Lummer-Brodhun is moved to obtain a balance for equal luminosity. Thus the device enables the total radiation of two sources to be compared with great sensitiveness in the same manner as a photometer screen allows the luminous radiation of two sources to be compared.

The surface bolometer has the advantages over the thermopile in being more sensitive, in being able to have the sensitiveness adjusted by varying the current through the bridge, in permitting a balance to be obtained, (giving a null method) by varying the resistance along a slide wire, and in having an exceedingly small thermal capacity and time lag as compared with a thermopile. The instrument may be modified to read radiation

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 22–3, 1910.

in absolute measure and hence become a pyrheliometer. It may be adapted for use as a sensitive and accurate sunshine recorder, and gives promise of being adapted for use as a radiation pyrometer. Slides will be shown fully explaining its construction and uses.

SOME PHOSPHORESCENT SALTS OF SODIUM WITH CADMIUM.[1]

BY C. W. WAGGONER.

IN an earlier work[2] the writer studied the phosphorescent decay of some simple compounds, among which was a compound of cadmium sulphate and manganese sulphate, made by simply evaporating to dryness a water solution of the two salts. On taking up this compound for further work a year later it was found that it had absorbed enough water from the atmosphere to destroy its phosphorescent properties, and it was necessary to drive off this water to cause it to regain its original properties of phosphorescence. On testing the original cadmium sulphate, in the anhydrous condition, from which the compounds had been made, it was found to give a yellow phosphorescence when excited by an ultra-violet source. A micro-chemical test showed the presence of a very small trace of sodium and zinc. Some phosphorescent-free cadmium sulphate was procured and a number of phosphorescent compounds were made by adding different salts of sodium to the cadmium sulphate.

From sixteen soluble salts of sodium which were tried, eleven produced phosphorescence when added to the cadmium sulphate. The color of the phosphorescence when excited by the ultra-violet from an iron spark, varied from blue to yellow depending upon the salt used.

With a new form of phosphoroscope decay curves were taken where the intensity was sufficient to measure with a spectrophotometer and the curves all show the same general characteristics as those determined for the $MnSo_4 - CdSO_4$ compounds in the paper referred to above.

The distribution of the energy in the phosphorescent spectrum was determined for $CdSO_4 + NaMnO_4$, $CdSO_4 + MnCl_2$, and $CdSO_4 + MnSO_4$. The curves show a decided similarity, giving the maximum value in all three at about $.566\mu$.

WEST VA. UNIVERSITY.

THE EFFECT OF TEMPERATURE ON THE IONIZATION OF A GAS.[1]

BY J. H. CLO.

THIS paper is an account of an attempt to measure the ionization of a gas at higher temperatures than have hitherto been investigated, and at the same time to obtain sufficient accuracy to detect any small

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 22–3, 1910.

[2] PHYS. REV., Vol. XXVII., p. 209, 1908.

variation due to change in temperature. The ionization was measured by the usual electrometer method, radium being used as the ionizing agent. It was found necessary to keep the density of the gas constant, in order to eliminate errors due to certain disturbances caused by change of density. As soon as the temperature at which the metallic electrodes began to give off electrons, was reached, it became necessary to eliminate this effect, partly by prolonged heating and partly by balancing the heat leak by means of an auxiliary chamber. Experiments were made on hydrogen and on air. No effect was noticeable. For hydrogen the ionization was constant to about 0.2 per cent. up to temperatures above 400° C., and for air the same uniformity was found to hold up to 500° C., while readings of almost the same constancy were taken in air up to 600° C.

UNIVERSITY OF CHICAGO.

THE INDUCTANCE OF A METAL TUBE BENT INTO THE FORM OF A CIRCULAR RING.[1]

BY F. W. GROVER.

AN approximate formula for the inductance of a circular ring with circular cross-section has been derived by applying Maxwell's principle of the geometric mean distance to the cross-section of the ring. The formula derived rests upon the assumption that the radius of cross-section is small in comparison with the mean radius of the ring. To obtain the correction due to the departure from this condition in any given case, Max Wien[2] derived a more exact expression by integrating over the cross-section of the ring Maxwell's series formula for the mutual inductance of two parallel, coaxial circles. Wien's expression corrected by Terezawa[3] for an error in the coefficient of ρ^2/R^2 is

$$L = 4\pi R\left[\left(1 + \frac{\rho^2}{8R^2}\right)\log\frac{8R}{\rho} - 1.75 + \frac{\rho^2}{24R^2}\right] \qquad (1)$$

where R = mean radius of the ring.

ρ = radius of the cross-section.

This expression was first given by Rayleigh[4] without proof. In this expression, all terms of the order of ρ^2/R^2 are included, which gives an accuracy ample for all practical cases. Formula (1) differs from Max-

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 22–3, 1910.

[2] Wied. Ann., 53, pp. 932–935, 1894.

[3] Tokyo Math. Phys. Soc. (2), 5, p. 84, 1909.

[4] Collected Papers, Vol. II., p. 15.

well's expression principally in the last term, the error being, however, negligible in most cases.

The author of this paper has employed Wien's method to obtain

1. The inductance of a circular ring whose cross-section is a circular line; that is, the practical case of a ring of circular cross-section traversed by a current of very high frequency. The inductance in this case is to the same order of accuracy as the preceding

$$L = 4\pi R\left[\left(1 + \frac{\rho^2}{4R^2}\right)\log\frac{8R}{\rho} - 2\right]. \qquad (2)$$

2. The general case of a circular ring whose cross-section is bounded by two concentric circles of radii r and ρ, that is, of a tube whose walls have a thickness $(\rho - r)$. For this case

$$L = 4\pi R\left[\left(1 + \frac{r^2+\rho^2}{8R^2}\right)\log\frac{8R}{\rho} - 1.75 - \frac{r^2}{2(\rho^2-r^2)} + \frac{2\rho^2+r^2}{32R^2} + \frac{r^4}{(\rho^2-r^2)^2}\left(1 + \frac{r^2}{8R^2}\right)\log\frac{\rho}{r} - \frac{\rho^4+r^2\rho^2+r^4}{48R^2(\rho^2-r^2)}\right]. \qquad (3)$$

For $\beta^2 = \rho^2 - r^2$ small in comparison with ρ we find on expanding (3)

$$L = 4\pi R\left[\left\{1 + \frac{\rho^2}{4R^2}\left(1 - \frac{1}{2}\frac{\beta^2}{\rho^2}\right)\right\}\log\frac{8R}{r} - 2 + \frac{1}{6}\frac{\beta^2}{\rho^2}\left(1 + \frac{3}{8}\frac{\rho^2}{R^2}\right) + \frac{\beta^4}{24\rho^4} + \cdots\right]$$

which for the limiting case of a tube with infinitely thin walls $\beta = 0$ is the same as (2) the expression already found for this case.

If $a = r/\rho$ is small, that is, if the cross-section is nearly solid, we find on expansion

$$L = 4\pi R\left[\left\{1 + \frac{\rho^2}{8R^2}(1 + a^2)\right\}\log\frac{8R}{\rho} - 1.75 + \frac{\rho^2}{24R^2} - \frac{a^2}{2}\left(1 + \frac{\rho^2}{48R^2}\right) - \frac{a^4}{2}\left(1 + \frac{\rho^2}{8R^2}\right) - a^4\log a - \cdots\right]$$

which when $a = 0$ (the case of a solid ring of circular cross-section) goes into (1) the equation of Rayleigh.

For a ring for which $R = 20$ cm., $\rho = 0.5$ cm. The inductance with varying values of the radius of the inner wall of the tube is

r cm.	L cm.	
0	1010.032	solid cross-section
0.125	1003.210	
0.250	987.528	
0.375	968.045	
0.500	947.308	infinitely thin walls

A Test Object for Photometry by Visual Acuity.[1]

By Herbert E. Ives.

ACUITY of vision, or the ability to distinguish detail, is sometimes used to measure illumination. Acuity is determined by means of test objects, of which there are two classes. With objects of the first class the illumination of the object is changed until certain detail is distinguished. With objects of the second class the illumination is taken as it occurs and the details observed are of different sizes, of continually varying size, or are changed in size by change of distance from the eye. Objects of both classes are open to objection, because memory, visual accommodation, retinal induction and psychological factors of recognition complicate the results. An ideal test object should possess details whose fineness could be changed uniformly, accompanied by no change in illumination, flux of light entering the eye, or distance.

These requirements are admirably met by a test object composed of two coarse transmission diffraction gratings laid one over the other. On rotation of one about an axis normal to their surfaces, broad dark bands appear whose separation changes uniformly and without the observer being cognizant of change until the bands reach the size necessary for visibility.

The distance of the bands from each other varies inversely as the chord of the angle. As the angle need vary only about 20 degrees, the chord and arc are practically the same, so that the visual acuity is directly as the angle between the grating lines.

A Graphic Recorder for Cooling Curves.[1]

By C. B. Thwing.

THE method consists in comparing the rate of cooling of the test piece with the rate of cooling of an adjacent neutral body. The instrument consists of two galvanometers recording on a single chart carried by one clock. The needles are depressed on the chart eight times per minute. The chart has two speeds, one of three fourths of an hour, one of one and one half hours. One galvanometer is attached to a thermocouple imbedded in close contact with the metal of the neutral body; the other measures the E.M.F. of a series of short thermocouples, one junction of which is imbedded in the neutral body, the other junction in the test piece. The size of the test piece need not exceed 25 mm. in length, and the same in diameter, having a cavity 8 mm. in diameter and 12 mm. deep.

The temperature range of the differential pyrometer is 50°, more or less as desired.

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 22-3, 1910.

INDEX TO VOLUME XXX.

A.

Absorption, The, of Limonene at Low Temperatures, *F. A. Molby* and *R. C. Gibbs*, 92.

Absorption, The, of Sodium Vapor, *Geo. B. Clinkscales*, 594.

Absorption of Roentgen Rays, The, *R. A. Millikan* and *E. J. Moore*, 131.

Absorption Spectrum, A Very Fine Band, Uranous and Uranyl Bands, *W. W. Strong*, 279.

Adams, E. P., On Contact Difference of Potential in a Magnetic Field, 371.

Allen, S. J., Radioactivity, On the Secondary β Radiation from Solids, Solutions and Liquids, 276.

Alloys, Magnetostriction in Iron-Carbon, *Herbert G. Dorsey*, 698.

Aluminum Rectifier, Effect of Pressure on the, *A. P. Carman* and *G. J. Balzer*, 776.

American Physical Society.
- Abstracts, 123, 262, 411, 782.
- Minutes, 122, 262, 532, 656.
- Treasurer's Report, 265.

Anthracene Vapor, The Electrical Conductivity of Fluorescent, *H. E. Howe*, 453.

Arc, Relation between Temperature of Electrodes and Voltage of the Electric, *C. D. Child*, 311.

Argon, A Quantitative Study of the Emission of Hydrogen, and Helium in the Visible Spectrum, *P. G. Nutting* and *Orin Tugman*, 661.

B.

Baker, Will C., "Bound Mass" and the Fitzgerald Lorentz Contraction, 634.

Balzer, G. J., Effect of Pressure on the Electrolytic Rectifier, 276, 776.

Barus, Carl, On the Probability of an Inherent Relation between the Electrical Resistance and the Hardness of Steel, 347.

Begeman, L., The Value of *e* by Wilson's Method, 131.

Bishop, F. L., The Heat of Dilution of Aqueous Salt Solution, 281.

Bolometer, A Special Form of Surface, for Total Radiation Experiments, *E. F. Northrup*, 785.

Book Reviews:
- Elements of Physics, *Crew* and *Franklin*, 292.
- Light, *Richard C. MacLaurin*, 291.
- Radiation, Light, and Illumination, *Charles P. Steinmetz*, 292.
- Text-Book of Physical Chemistry, *Arthur W. Ewell*, 292.
- Electric Waves, *W. S. Franklin*, 292.
- Dynamos and Motors, *Wm. S. Franklin* and *William Esty*, 292.
- Dynamo Laboratory Manual, *Wm. S. Franklin* and *William Esty*, 292.
- The Alternating Current Commutator Motor and the Leakage of Induction Motors, *Rudolf Goldschmidt*, 292.
- The Evolution of Worlds, *Percival Lowell*, 292.

Black Radiation, On the Thermodynamics of, *Paul Saurel*, 350.

Blake, F. C., On the Extra Transmission of Electric Waves, 674.

Bragg, W. H., The Secondary Radiation Produced by the Beta Rays of Radium, 638.

Bridgman, P. W., The Freezing of Mercury at High Pressures, 275.

Bunsen Flame, Temperature of the Divided, *Daniel W. Shea*, 397.

Burnett, E. S., On a Radial Flow Porous Plug and Calorimeter, 529.

C.

Cadmium Cells, Polarization of, *R. R. Ramsey*, 128.

Calorimeter, On a Radial Flow Porous Plug and, *E. S. Burnett* and *J. R. Roebuck*, 529.

Canary Glass, Fluorescence and Absorption of, at Low Temperatures. The Effect of Temperature on Fluorescence and Absorption, II., *R. C. Gibbs*, 377.

Capillary Tube, The Flow of a Gas through a, *Willard J. Fisher*, 269.

Carman A. P., Effect of Pressure on the Electrolytic Rectifier, 276, 776.

Cathode Equilibrium, The, in the Weston Standard Cell, *G. A. Hulett*, 648.

Cathode Rays, The Variation with Velocity of e/m for, *C. A. Proctor*, 53.

Chapman, E. K., Note on the Cause of the Discrepancy between the Observed and the Calculated Temperatures after Expansion in the Space between the plates of a Wilson Expansion Apparatus, 286.

Child, C. D., Relation between Temperature of Electrodes and Voltage of the Electric Arc, 311.

Circular Dividing Engine, An Automatic, *W. R. Stamper* and *Elmer E. Hall*, 492.

Clifford, O. C., Magnetic Properties of Heusler Alloys, 125.

Cline, G. A., On the Penetrating Radiation at the Surface of the Earth, 35.

Clinkscales, Geo. B., The Absorption of Sodium Vapor, 594.

Clo, J. H., The Effect of Temperature on the Ionization of a Gas, 786.

Coblentz, W. W., Note on Water of Crystallization, 322.

Note on the Reflecting Power of Tantalum, Tungsten, and Molybdenum, 645.

Colby, Walter F., The Coefficient of Expansion of Nickel near its Critical Temperature, 506.

Comstock, D. F., A Neglected Type of Relativity, 267.

Compton, Karl T., A Study of the Wehnelt Electrolytic Interrupter, 161.

Conductivity, The Electrical, of Fluorescent Anthracene Vapor, *H. E. Howe*, 453.

Contacts, Neutral, and Switches, *Walter P. White*, 784.

Critical Temperature, The Coefficient of Nickel near its, *Walter F. Colby*, 506.

Crystallization, Note on Water of, *W. W. Coblentz*, 322.

D.

Day, Arthur L., The Nitrogen Thermometer from Zinc to Palladium, 412.

Dorsey, Herbert G., Coefficients of Linear Expansion at Low Temperatures, 271.

Magnetostriction in Iron-carbon Alloys, 698.

E.

Earhart, Robert F., The Rectifying Effect in Point and Plane Discharge, 275.

The Rectifying Effect in the Point and Plane Discharge, 460.

Electric Wave Receivers, *Harold W. Webb* and *L. E. Woodman*, 192.

Electric Waves, A Study of the Multiple Reflections of Short, between two or more Reflecting Surfaces, 561.

Electrical Oscillator, The Wave-Length and Overtones of a Linear, *James E. Ives*, 199.

Electrical Resistance, Temperature Coefficients of, *A. A. Somerville*, 268.

Electrical Resistance, On the Probability of an Inherent Relation between the, and the Hardness of Steel, *Carl Barus*, 347.

Electrolytic Iron, The Effect of Temperature on the Magnetic Properties of, *Earle M. Terry*, 127, 133.

Electrolytic Rectifier, The Effect of Pressure on the, *A. P. Carman* and *G. J. Balzer*, 276.

Electrolysis, Minute Phenomena of, *H. W. Morse*, 272.
Entladungsstrahlen, Ionization produced by, and Experiments bearing on the Nature of the Radiation, *Elizabeth R. Laird*, 293.
Entropy, On, *W. S. Franklin*, 766.
Electric Waves, On the Extra Transmission of, *F. C. Blake*, 674.
Elastic, The, Properties of Platinum-Iridium Wires, *K. E. Guthe* and *L. P. Sieg*, 610.
Ether, The Relative Motion of the Earth and the, *H. A. Wilson*, 411.
Expansion, Coefficients of Linear, at Low Temperatures, *Herbert G. Dorsey*, 271.
Expansion, The Coefficient of, of Nickel near its Critical Temperature, *Walter F. Colby*, 506.
Expansion, The, of Fused Quartz at High Temperatures, *H. M. Randall*, 216.

F.

Fluorescence Spectra, The Distribution of Energy in. Studies in Luminescence, XI., *E. L. Nichols* and *Ernest Merritt*, 328.
Fluorescence and Absorption, The Effect of Temperature on, II., Fluorescence and Absorption of Canary Glass at Low Temperatures, *R. C. Gibbs*, 377.
Fisher, Willard J., The Flow of a Gas through a Capillary Tube, 269.
Fitzgerald Lorentz Contraction, "Bound Mass" and the, *Will C. Baker*, 634.
Franklin, W. S., On Entropy, 766.

G.

Gage, O. Amsden, The Point Discharge in Air for Pressures Greater than Atmospheric, 720.
Galvanometer, The Relation between Zero Shift and Size of Wire in the Moving Coil, *Walter P. White*, 782.
Galvanometer, The Theory of the Vibration, *F. Wenner*, 274.
Gas, The Effect of Temperature on the Ionization of a, *J. H. Clo*, 786.
Gibbs, R. C., The Effect of Temperature on Fluorescence and Absorption, II., Fluorescence and Absorption of Canary Glass at Low Temperatures, 377.
The Absorption of Limonene at Low Temperatures, 92.
Gowdy, R. C., The Fatigue of Metals subjected to the Roentgen Radiation, 62.
Graphic Recorder, A, for Cooling Curves, *C. B. Thwing*, 789.
Grover, F. W., The Inductance of a Metal Tube Bent into the Form of a Circular Ring, 787.
Guthe, K. E., The Elastic Behavior of Platinum-Iridium Wire, 132.
Radioactivity, The Elastic Properties of Platinum-Iridium Wires, 610.

H.

Hall Effect, The Variation of the, in Metals with Change of Temperature, *Alpheus W. Smith*, 1.
Hall, Elmer E., An Automatic Circular Dividing Engine, 492.
Ham, Wm. R., Polarization of Roentgen Rays, 96.
Heat of Dilution, The, of Aqueous Salt Solution, *F. L. Bishop*, 281.
Helium, A Quantitative Study of the Emission of Hydrogen, Argon, and, in the Visible Spectrum, *P. G. Nutting* and *Orin Tugman*, 661.
Heusler Alloys, Magnetic Properties of, *A. A. Knowlton* and *O. C. Clifford*, 125.
Heusler Alloys, Magnetic Properties of, *E. B. Stephenson*, 127.
Heusler Alloys, Preparation and Properties of the, *A. A. Knowlton*, 123.
Howe, H. E., The Electrical Conductivity of Fluorescent Anthracene Vapor, 453.
Hubbard, J. C., Physical Properties of Binary Liquid Mixtures, 740.
Physical Properties of Binary Liquid Mixtures, 284.
On the Use of Polar Coördinates in Thermodynamics, 284.

Huff, W. B., Typical Cases of Secondary Radiation Excited by Uranium-X, 482.

Hulett, G. A., The Cathode Equilibrium in the Weston Standard Cell, 648.

Hydrogen, A Quantitative Study of the Emission of, Argon, and Helium in the Visible Spectrum, *P. G. Nutting* and *Orin Tugman*, 661.

I.

Inductance, The, of a Metal Tube Bent into the Form of a Circular Ring, *F. W. Grover*, 787.

Ingersoll, L. R., A Method of Determining the Optical Constants of Metals Applicable to Measurements in the Infra-red Spectrum, 130.

Infra-red Spectrum, A Method of Determining the Optical Constants of Metals Applicable to Measurements in the, *L. R. Ingersoll*, 130.

Ionization produced by Entladungsstrahlen and Experiments bearing on the Nature of the Radiation, *Elizabeth R. Laird*, 293.

Ions, The Effect of Changes in the Pressure and Temperature of Gases upon the Mobility of the Negative, Produced by Ultra-violet Light, *Alois F. Kovarik*, 415.

Iron, The Absolute Values of the Moments of the Elementary Magnets of, Nickel and Magnetite, *Jakob Kunz*, 359.

Ives, Herbert E., A Test Object for Photometry by Visual Acuity, 789.

Scattered light in Spectrophotometry and a New Form of Spectrophotometer, 446.

The Photographic Evidence for Dispersion of Light in Space — Is it a Purely Photographic Phenomenon? 272.

Ives, James E., The Wave-length and Overtones of a Linear Electrical Oscillator, 199.

K.

Knipp, Chas. T., A Convenient Form of Quartz Tube Mercury Lamp, 641.

Knowlton, A. A., Preparation and Properties of the Heusler Alloys, 123.

Magnetic Properties of Heusler Alloys, 125.

Kovarik, Alois F., The Effect of Changes in the Pressure and Temperature of Gases upon the Mobility of the Negative Ions Produced by Ultra-Violet Light, 415.

Kunz, Jakob, The Absolute Values of the Moments of the Elementary Magnets of Iron, Nickel, and Magnetite, 359.

Kunz, Jakob, The Absolute Value of the Moments of Elementary Magnets, 131.

L.

Lake, Chas. H., The Rectifying Effect in the Point and Plane Discharge, 460.

The Rectifying Effect in Point and Plane Discharge, 275.

Laird, Elizabeth R., Ionization produced by Entladungsstrahlen and Experiments bearing on the Nature of the Radiation, 293.

Lepel Singing Arc, Experiments in Impact Excitation with the, *G. W. Nasmyth*, 281.

Limonene, The Absorption of, at Low Temperatures, *F. A. Molby* and *R. C. Gibbs*, 92.

Limonene, The Rotary Power of, at Low Temperatures, *F. A. Molby*, 77.

Liquid Mixtures, Physical Properties of Binary, *J. C. Hubbard*, 740.

Luminescence, Studies in, XI., The Distribution of Energy in Fluorescence Spectra, *E. L. Nichols* and *Ernest Merritt*, 328.

Lyman, Theodore, The Spectra of Some Gases in the Region of Extremely Short Wave-Length, 268.

M.

McDaniel, A. S., The Effect of Filter Paper upon the Mass and Form of the Deposit in the Silver Coulometer, 658.

McDowell, Louise S., Some Electrical Properties of Selenium, II., The Recovery from Excitation by X-Rays, 474.

McKeehan, L. W., An Improved Form of Volumenometer, 189.

The Terminal Velocity of Fall of Small Spheres in Air, 535.

McLennan, J. C., Note on the Coefficients of Diffusion of the Emanation and the Active Deposit Particles of Actinium, 660.

Magnets, The Absolute Value of the Moments of Elementary, *Jakob Kunz*, 131.

Magnets, The Absolute Values of the Moments of the Elementary, of Iron, Nickel, and Magnetite, *Jakob Kunz*, 359.

Magnetization Curves for a Sample of Iron One Mil in Diameter, *J. A. Veazey*, 180.

Magnetic Field, On Contact Difference of Potential in a, *E. P. Adams*, 371.

Magnetostriction in Iron-Carbon Alloys, *Herbert G. Dorsey*, 698.

Magnetite, The Absolute Values of the Moments of the Elementary Magnets of Iron, Nickel and, *Jakob Kunz*, 359.

Marvin, C. F., Note on the Relation between the Temperature and the Resistance of Nickel, 522.

Marvin, C. F., Note on the Relation between the Resistance of Nickel and the Temperature, 658.

The Use of the Electrical Resistance Thermometer in Apparatus for the Absolute Measurement of Solar Radiation, 657.

Melde's Experiment, Some Curious Phenomena Observed in Connection with, *J. S. Stokes*, 659.

Merritt, Ernest, Studies in Luminescence, XI., The Distribution of Energy in Fluorescence Spectra, 328.

Mercury Lamp, A Convenient Form of Quartz Tube, *Chas. T. Knipp*, 641.

Millikan, R. A., The Absorption of X-rays an Additive Property, 131.

Some New Values of the Potentials Assumed by Metals in a High Vacuum under the Influence of Ultra-violet Light, 287.

Note on the Cause of the Discrepancy between the Observed and the Calculated Temperatures after Expansion in the Space between the Plates of a Wilson Expansion Apparatus, 286.

Molby, F. A., The Rotary Power of Limonene at Low Temperatures, 77.

The Absorption of Limonene at Low Temperatures, 92.

The Rotatory Dispersion of Quartz at —190° and Observations at other Temperatures, 273.

Molybdenum, Note on the Reflecting Power of Tantalum, Tungsten, and, *W. W. Coblentz*, 645.

Moody, H. W., Note on the Cause of the Discrepancy between the Observed and the Calculated Temperatures after Expansion in the Space between the Plates of a Wilson Expansion Apparatus, 286.

Moore, E. J., The Absorption of X-rays an Additive Property, 131.

Morse, H. W., Minute Phenomena of Electrolysis, 272.

N.

Nasmyth, G. W., Experiments in Impact Excitation with the Lepel Singing Arc, 281.

Nichols, E. L., Studies in Luminescence, XI., The Distribution of Energy in Fluorescence Spectra, 328.

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ERRATA.

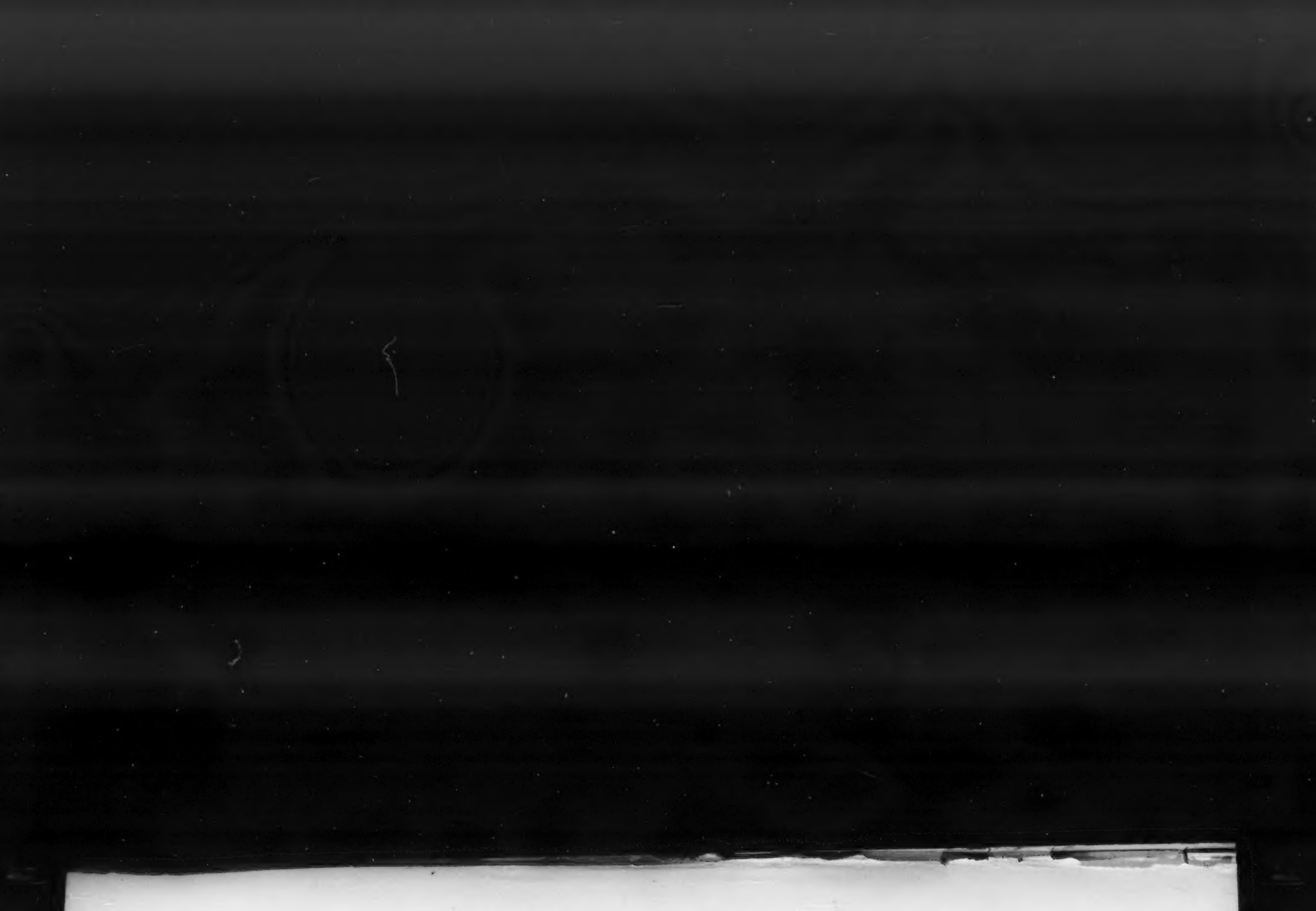
Page 342. The equation a little above the middle of the page, which now reads

$$L_1 = \frac{2ma}{d_1^2}\left[2cf + \frac{a(c-a^2+2c^2)}{3}f''\right]$$

should read

$$L_1 = \frac{2ma}{d_1^2}\left[2cf + \frac{c(a^2+c^2)}{3}f''\right]$$

the expression being the same as that found when $a > c$.



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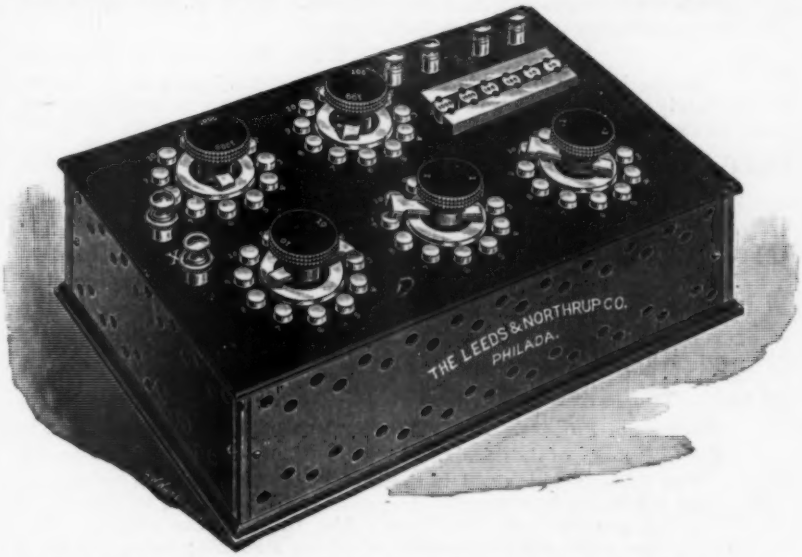

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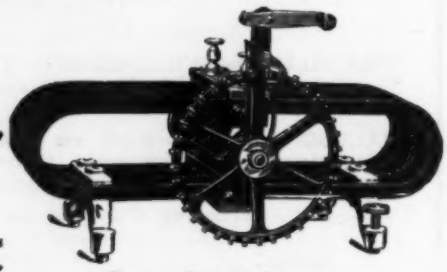

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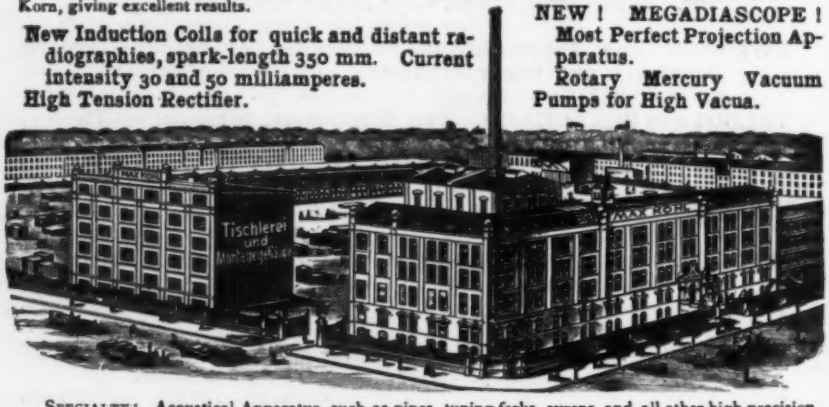

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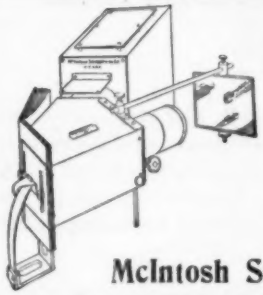

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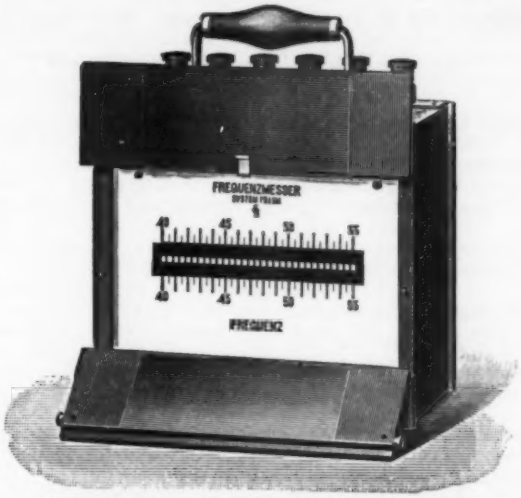

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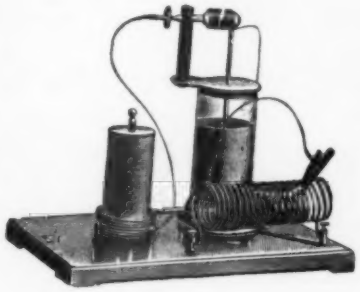

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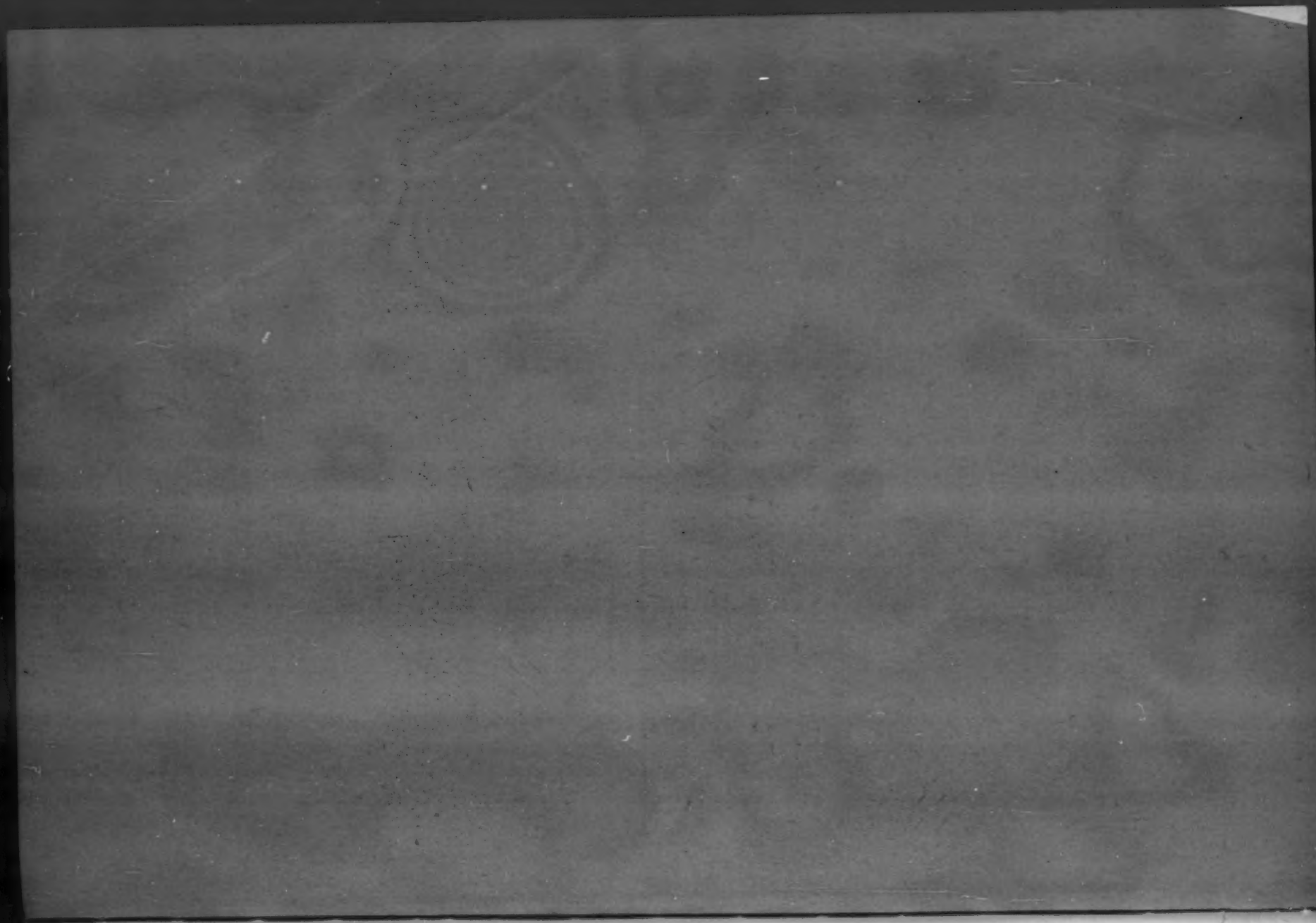

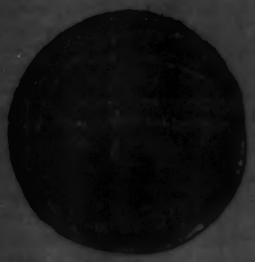

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